

SPECIFICATION

REACTIVE MONOMER COMPOSITION MODIFIED
BY A SMALL-AMOUNT OF LACTONES, AN ACRYLIC POLYOL RESIN,
A CURABLE RESIN COMPOSITION, AND A COATING COMPOSITION

TECHNICAL FIELD

The present invention I relates to a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones in which there is decreased the amount of adducts containing two or more continuous lactone chains, a method for the preparation thereof, and an acrylic polyol resin which can be employed as an industrial finishing agent having a high quality and which is variously well-balanced, for example, coatings and a pressure-sensitive adhesive, an ultraviolet ray- or electron beam-curable coating agent, and a reactive modifier.

Further, the present invention II relates to a method for the preparation of a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones.

Still further, the present invention III relates to a curable resin composition comprising an acrylic polyol resin containing the hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones as a polymerizable component and a melamine resin, by which there can be prepared a coating having an improved acid resistance and being well-balanced in abrasion resistance and an acid resistance.

Furthermore, the present invention IV relates to a melamine-curable type water-based coating composition comprising the acrylic polyol resin containing the hydroxyalkyl(meth)acrylate

composition modified by a small amount of lactones and an amino-plasto resin, and which is appropriate as a water-based coating for cars, home electric appliances, and cans for beverages and foods, particularly, which is appropriate as a clear coating for finishing an outer surface of cans.

In addition, the present invention V relates to a curable resin composition containing an acrylic polyol resin obtained by employing the hydroxyalkyl (meth) acrylate composition modified by a small amount of lactones in which there are decreased adducts containing two or more continuous lactone chains and a polyisocyanate compound as essential components, by which there can be prepared a coating having a long pot life and an excellent abrasion resistance and water resistance.

Also, the present invention VI relates to a coating containing a curable resin composition and crosslinked particles obtained from the curable resin composition or urethane-urea/ethylenic resin-composite type crosslinked particles as essential coating layer-formable components. The curable resin composition essentially contains a hydroxyalkyl (meth) acrylate composition modified by a small amount of lactones and a polyisocyanate compound as essential components. The hydroxyalkyl (meth) acrylate composition is a vinyl-based copolymer having carboxylic group and a crosslinkable functional group. The vinyl-based copolymer is obtained by allowing to react the hydroxyalkyl (meth) acrylate composition (a) modified by a small amount of lactones with a carboxylic group-contained vinyl-based monomer and other vinyl-based monomers.

The vinyl-based copolymer is the acrylic polyol resin (A) in the

curable resin composition of the present invention V.

And also, the present invention VII relates to a thermosetting resin composition comprising an acrylic polyol resin containing the hydroxyalkyl (meth)acrylate composition modified by a small amount of lactones and an alkoxysilyl group-contained acrylic copolymer, and relates to a top-coat clear coating primarily containing the thermosetting resin composition, and which is employed as an outer coating for buildings, a variety of coatings for cars, industrial machines, a steel-made furniture, home electric appliances, and plastics, in which durability is particularly required.

Besides, the present invention VIII relates to a carboxylic group-contained acrylate modified by a small amount of lactones which is useful as a raw material for resins.

Also, the present invention IX relates to a curable resin composition, a clear coating composition, and a method for coating, and the curable resin composition is employed as a finishing coating for cars and coil coating, etc., which is composed of an acrylic polycarboxylic acid resin containing a carboxylic group-contained acrylate monomer modified by a small amount of lactones and a polyepoxide.

And also, the present invention X relates to a polyester unsaturated monomer composition modified by a small amount of lactones, a method for the preparation thereof, and an acrylic resin prepared therefrom which does not show tackiness.

By allowing to react these monomer compositions with other ethylenic unsaturated monomer and formulating with a variety of crosslinking agents and other components which are usually employed,

there can be prepared an industrial finishing agent which is variously well-balanced, for example, a coating, an pressure-sensitive adhesive, an ultraviolet ray- or electron beam-curable coating agent, a curable oligomer and a polymer which can be employed as a reactive modifier, etc.

BACKGROUND ART

I and II.

In recent years, there has been raised an importance of an acrylic-based coating in a coating field.

It is a reason that it has an excellent characteristic in weatherability, chemical resistance, and staining resistance, etc. compared to other alkyd resins, polyester resins, and epoxy resins.

For that reason, an acrylic-based coating has been employed in many fields such as cars, home electric appliances, metals, and construction materials.

Of acrylic resins, an acrylic polyol in which a monomer having hydroxyl group is copolymerized is applied as an ordinary temperature-curable coating or a baking-curable coating in which there is formulated a crosslinking agent which is capable of reacting with hydroxyl group, for example, a polyisocyanate and a melamine resin, etc. The monomer having hydroxyl group is indispensable in order to give adhesion to a coating layer and a gasoline resistance.

As the monomer having hydroxyl group, there have been conventionally employed a hydroxyethyl(meth)acrylate and hydroxypropyl(meth)acrylate, etc. Herein, the (meth)acrylate means an acrylate and a methacrylate.

However, hydroxyl groups in an acrylic polyol prepared by copolymerization of the monomers do not show a sufficient reactivity with the crosslinking agent because it is situated in a position which is exceedingly near by a main chain of a rigid acrylic resin skeleton.

For the purpose of improvement thereof, although 4-hydroxybutylacrylate is proposed, it is difficult to say that reactivity thereof is sufficient.

In order to solve problems, there has been employed a means for synthesizing a lactone-modified acrylic polyol in which ϵ -caprolactone is allowed to addition-react to a hydroxyalkylacrylate or a hydroxyalkylmethacrylate, followed by copolymerizing with other monomers.

By the means, although reactivity with the crosslinking agent and ductility can be solved, a distribution of lactone continuous chains is broad in a conventional lactone-modified (meth)acrylate, and the number (n) of the lactone continuous chains becomes large and, whereby, although curing reactivity and ductility are improved, there is occasionally caused a problem that there lower hardness and acid resistance, etc.

For example, in the case that there is employed a hydroxyalkylacrylate or a hydroxyalkylmethacrylate having the large number of the lactone continuous chain in which ϵ -caprolactone is added as a raw material in a top-coat coating for cars, since a hydroxyl value per the unit weight of a product becomes lower, a large amount of the acrylate or methacrylate must be employed in order to adjust the hydroxyl value, whereby, there are occasionally deteriorated other requiring items such as a glossiness and an acid resistance other than

the abrasion resistance.

Further, although it is occasionally controlled using a hydroxyethylacrylate or hydroxyethylmethacrylate in order to adjust the hydroxyl value without feeding a large amount of a lactone-modified hydroxyalkylacrylate or hydroxyalkyl methacrylate, in the case, there becomes smaller a proportion of a hydroxyalkyl(meth)acrylate containing 1 mol of the lactone single chain in which the number of "n" is 1, in which ductility and hardness are well-balanced.

III.

In a coating layer for cars, it is looked upon that there are problematic a durability of the coating layer, particularly, blurs by acidic rain, scratches caused by sand particles which are blown up by a washing brush and by running. For example, a clear coat which is an over-coating in a car body is often composed of an acrylic resin and a melamine resin, and it becomes clear that the melamine resin causes a problem of decline in the acid resistance and, there are proposed (JP-A-63221123 Official Gazette and JP-A-63108048 Official Gazette) coatings by a novel crosslinking style not containing the melamine resin. However, the coatings are higher in price compared to a melamine-based thermosetting coating, and include a problem that those are poor in adhesion to the melamine-based thermosetting coating.

Of the acrylic resins, an acrylic polyol in which there is copolymerized a monomer having hydroxyl group is employed in an ordinary temperature-curable or thermosetting-curable coating in which there is formulated a crosslinking agent which can react with hydroxyl group, for example, such as a polyisocyanate and a melamine resin. In order to give an adhesion to a coating layer and a gasoline resistance, acrylic

monomers having hydroxyl group are indispensable.

As such the monomers having hydroxyl group, there have been conventionally employed a hydroxyethyl(meth)acrylate and a hydroxypropyl(meth)acrylate, etc.

However, since the hydroxyl group in an acrylic polyol prepared by copolymerization of the (meth)acrylates is situated in an exceedingly near position to a main chain of an acrylic resin structure which is rigid, a reactivity with the crosslinking agent is not sufficient.

For the purpose of improvement thereof, although 4-hydroxybutylacrylate is proposed, it is difficult to say that a reactivity thereof is sufficient.

As a method for solving such the problems, in relation to a abrasion resistance, for example, there has been conventionally known (JP-A-64066274 Official Gazette) a coating using a clear coat in which there are employed an ϵ -caprolactone-modified acrylic resin obtained by copolymerization of an ϵ -caprolactone-added hydroxyalkyl(meth)acrylate with other vinyl monomers and a melamine curing agent and, further, for an acidic rain, for example, there has been conventionally known (JP-A-04114069 Official Gazette) a coating using a clear coat in which there are simultaneously employed a reaction of carboxylic acid with an epoxy and a reaction of an acrylic resin with a melamine curing agent.

However, since the lactone-modified (meth)acrylate in a technology of the JP-A-64066274 Official Gazette has a broad distribution of continuous lactone chains and the number (n) of the continuous lactone chains is large, there is occasionally caused the above-described problem that although curing reactivity and

flexibility are improved, there lower hardness and acid resistance, etc.

On the other hand, although there is obtained a coating layer having an excellent acid resistance in a technology of the JP-A-04114066 Official Gazette, abrasion resistance is insufficient.

Further, there has been known that it is an effective method to elevate a glass transition temperature in a cured coating layer formed from a clear coat which is a most outside surface layer in order to obtain an advanced acid resistance. However, in the case, there has been a problem that there is caused an unpreferred situation that there lower not only the abrasion resistance in the coating layer but also flexural resistance and adhesion in recoating. Accordingly, it has been an exceedingly difficult technology to obtain a coating layer which is highly well-balanced in the acid resistance and abrasion resistance, and which is also excellent in the flexural resistance and adhesion in recoating.

IV.

Metal cans have been widely employed as a vessel for filling a variety of beverages and foods.

Outside surface of the cans is coated in order to prevent corrosion by outside circumstances, and printed in view of a fine sight, and for showing contents. In printing and coating of the outside surface of the cans, a size-coating is coated on a metal plate, and then, a white coating is coated and, printing is conducted thereon by inks, etc. and a clear coating is coated for finishing. The size-coating and white coating are also occasionally omitted. Hitherto, as the clear coating for finishing, there has been widely employed an organic solvent

solution containing an acrylic/amino-based resin, a polyester/amino-based resin, and an epoxy/amino-based resin, etc.

JP-A-06207137 Official Gazette discloses a water-based coating for an outer surface of cans, which is a coating primarily containing a resin mixture composed of (A) 40-60 parts by weight of an acrylic resin having a specified composition which has a weight average molecular weight of 6,000-15,000 and a glass transition temperature of exceeding 0°C, (B) 10-20 parts by weight of an acrylic resin having a specified composition which has a weight average molecular weight of 5,000-50,000 and a glass transition temperature of not more than 0°C, and (C) 20-50 parts by weight of an amino-plasto resin, and the resins (A) and (B) are neutralized by a base and, the resins (A), (B), and (C) are dissolved or dispersed in water. However, a coating layer obtained from the above-described technology is not sufficient in hardness.

Publicly-known water-based coatings include two types of a water-dispersed type one and a water-soluble type one, and since the water-dispersed type one is usually synthesized by an emulsion polymerization method using a surface active agent, there has been a problem that the surface active agent remains in a coating layer after having formed the coating layer, and it causes a decline of water resistance. On the other hand, although there is also a method synthesizing a resin containing carboxylic groups in an organic solvent system without employing the surface active agent and making dispersible or water-soluble by neutralizing in a volatile base, the water-based coating requires an acidic component having an acid value of not less than 20 in a basic resin structure, and there has been a drawback of

poor water resistance and alkali resistance, etc.

A variety of coatings have been proposed and, although there is observed an improvement of water resistance in a coating layer, properties are not in a level being resistible to a thermally sterilizing treatment (retorting) in 130°C for 30 minutes.

JP-A-07316489 Official Gazette discloses a water-based coating composition characterized by containing 20-80 parts by weight of a water-based acrylic resin obtained by copolymerization of (i) α , β -ethylenic unsaturated carboxylic acid, (ii) a hydroxyl group-contained mono(meth)acrylate including an ϵ -caprolactone-modified monomer, (iii) an N-alkoxymethyl(meth)acrylic amide having an alkyl group of a carbon number of not more than 4, and an aromatic vinyl monomer which is copolymerizable with the (i)-(iii) and/or an alkyl(meth)acrylate and 10-60 parts by weight of a water-based amino resin. However, water resistance is not sufficient in the coating composition obtained by the above-described technology.

Further, a water-based coating composition has been also employed for coating in cars and home electric appliances.

For example, in recent years, a design value in resin-made parts such as a bumper for cars is elevated by coating the same color as in car bodies. In the case of coating a bumper made from a polypropylene, etc. like a body color, there is firstly coated a primer made from a chlorinated polypropylene, etc. in order to ensure adhesion. A coating layer is formed by a two coating-one baking method (hereinafter, referred to as a 2C1B method) in which a coating layer of the primer is thermally cured and a coating for a base coat and an over coating are coated by a wet-on-wet method and those are thermally cured

collectively.

However, there has become problematic a staining in a coating layer which is called a rain-blot under the influence of an acidic rain in recent years. Particularly, in a baked coating layer made from a melamine resin, it is known that an ether bond in the vicinity of melamine is broken by the acidic rain, and a stain penetrates therein, resulting in that it becomes difficult to remove the stain by a water-washing level. Accordingly, it must be rubbed off by a compound, etc. and, in the case, there is a problem that a coating layer is also shaved off, resulting in that the thickness of the coating layer becomes thinner.

Comparing a coating layer on an outside plate of cars to a coating layer on a bumper, the rain-blot is more readily caused in the coating layer on a bumper, there is a problem that the rain-blot once caused is not apt to be removed compared to the coating layer on an outside plate. It is thought that it depends upon a crosslinking density. In other words, since the coating layer on an outside plate is cured by heating conditions such as 140°C for 30 minutes or so, a crosslinking density is high. However, in the coating layer on a resin-made bumper, since heating temperature is suppressed in 120°C for 20 minutes or so in order to prevent deformation, a crosslinking density becomes lower compared to the coating layer on an outside plate for cars. For that reason, an acid rain resistance is not sufficient, and it is thought that the above-described difference is caused.

Therefore, it is thought that a blocked polyisocyanate compound is employed as a crosslinking agent without using a melamine resin. However, curability is poor at a low temperature in a coating composition

in which the blocked polyisocyanate compound is employed as a crosslinking agent. For that reason, when the coating composition is coated on a resin-made bumper, etc., since heating temperature is 120°C to the utmost, crosslinking density is low, resulting in that there become insufficient physical properties such as solvent resistance, staining resistance, and water resistance.

JP-A-11012533 discloses a water-based coating composition comprising a neutralized product of an amino resin-modified polymer in which structural units based on the above-described component (a) in the copolymer composed of (a) radically polymerizable compound having a specified structural formula, (b) an α, β -ethylenic unsaturated carboxylic acid, and (c) other radically polymerizable monomers are modified by a reaction of hydroxyl group in the units with an amino resin. However, a coating layer from the composition is not sufficient in retort resistance.

V.

As described hereinabove, in recent years, an acrylic-based coating is becoming important in a coating field and, in a coating layer for cars, durability of a coating layer, particularly, there become problematic a rain-blot by an acidic rain, abrasions by sand particles blown up by a washing brush and during driving, and the above-described various methods are proposed. However, there have still been the above-described various problems.

On the other hand, although an isocyanate curing system shows an excellent acid resistance, adhesion, water resistance, and hardness, there is a problem that a pot-life is shorter compared to a melamine coating and, crosslinking of a resin is insufficient, and abrasion

resistance is lower in a coating layer. Although the abrasion resistance can be improved by employing a modified hydroxy(meth)acrylate, etc. (PCL F, etc.), a pot-life further becomes short by an existing PCL F having a long lactone continuous chain length, and there is caused a problem that it cannot become taken a working time of period.

VI.

For the above-described problems in an isocyanate curing system, JP-A-05148313 Official Gazette proposes a coating which possesses various properties such as profitability and workability without loss of a fine spectacle and, moreover, which can also satisfy a corrosion resistance, and which can provide a coating layer for a metal having an advanced corrosion resistance and, moreover, which primarily contains a coating layer-formable resinous component in which there are employed specified crosslinked particles which do not cause any problems in corrosion resistance even though a conventional melamine curing agent is employed. Although the abrasion resistance can be improved by employing a modified hydroxy(meth)acrylate, etc. (PCL F, etc.), the abrasion resistance, the improvement is insufficient by the PCL F having a long lactone continuous chain length.

VII.

In a conventional thermosetting coating, there has been employed a melamine resin such as an alkyd melamine resin, an acrylic melamine resin, and an epoxy melamine resin as a crosslinking agent, and an odor from the melamine resin has been largely problematic. Further, in an acrylic melamine resin and an alkyd melamine resin which are usually employed as a coating for cars, there are not always sufficiently satisfied properties such as weatherability, staining resistance,

acidic resistance, and a water-repellent property, and an improvement thereof is strongly desired.

As a method for solving the problems, there is proposed a technology (JP-A-01141952 Official Gazette, etc.) concerning a composition which is cured by a crosslinking style using a polyol resin and a hydrolyzable silyl group-contained resin, and which is quite different from a crosslinking style using a conventional polyol resin and melamine resin. However, there are not still sufficiently satisfied hardness, abrasion resistance, water resistance, and solvent resistance.

VIII.

Since a polyalkyleneglycol di(meth)acrylate forms a flexible thin layer after curing, it is one of exceedingly useful raw materials for employing as an ink and coating, etc. Further, a low molecular weight one is important also as a reactive diluent in an acrylic resin field.

It is to be noted that in the present invention, an acrylate and methacrylate are called a (meth)acrylate, and acrylic acid and methacrylic acid are called a (meth)acrylic acid. However, an acrylic resin and a methacrylic resin are merely called an acrylic resin.

On the other hand, an acrylic resin having carboxylic group ($-COOH$) is effective for improving adhesion to a material which includes a resin such as a nylon having amino group, and an inorganic compound such as a metal having hydroxyl group and a silica. Further, it is recognized that it is effective for improving a water-solubility and an aqueous alkali solution-solubility of an acrylic resin, above all, shortening of developing time of period in an alkali development step and a removing ability of uncured portion in the case of forming a pattern using ultraviolet ray-curability.

For that reason, there is desired a carboxylic group-contained acrylate such as a carboxylic group-contained lactone acrylate, and there has been desired a method for the preparation thereof which is industrially and readily operated.

IX.

In a binder for employing as an over-coating for cars, a polymer having hydroxyl group is usually employed in combination with a melamine resin curing agent. However, in a cured thin layer obtained by employing a melamine resin as a curing agent, an acid resistance is usually poor. Accordingly, such the thin layer is apt to be particularly deteriorated by an acidic rain which is recently talked about, resulting in that a problem is caused in an outer appearance.

It is thought that a poor acid resistance in a thin layer obtained by employing a melamine resin as a curing agent is caused by a triazine ring in the melamine resin. Accordingly, so far as a melamine resin is employed as a curing agent, a drawback of the poor acid resistance is not solved.

For example, JP-A-02045577 and JP-A-03287650 Official Gazettes propose a novel coating composition in which a melamine resin is not employed. In the coating composition, since a crosslinking is initiated in an ester bond which is produced by a reaction of an acid group with an epoxy group, an acid resistance is excellent.

However, in the curing system, since functional group concentration is higher and viscosity is high, it is difficult to prepare a high solid type coating having a high solid content, and it is required that a large amount of solvents are employed.

On the other hand, in recent years, there is desired a high solid

coating which does not emit a large amount of solvents in circumstances in order to reduce a bad influence to circumstances.

JP-A-06166741 Official Gazette discloses a high solid coating composition in which a silicone polymer is employed. However, in the inventions, in order to introduce a hydroxyl group-functional silicone polymer into a coating composition, an acid-functionality is given by a reaction with an acid anhydride. As a result, there is caused a drawback that an amount of functional groups cannot be elevated, and Tg is lowered in resins and, Tg cannot be elevated in a coating layer.

On the other hand, JP-B-94041575 Official Gazette discloses a high solid coating composition containing (a) a polyepoxide and (b) a polyester polycarboxylic acid. However, solid content in the coating composition is not high from a viewpoint of not adversely affecting to circumstances, resulting in that a coating layer formed is poor in an acid resistance

Further, in an acid-epoxy curing type coating system, a clear coating layer when being thermally cured remarkably yellows compared to a conventional melamine type coating system, and it is difficult to design a light color such as a white mica color.

X.

As described hereinabove, in recent years, an acrylic-based coating is becoming important in a coating field, and an acrylic-based coating is becoming employed in every fields.

In a conventional lactone modified (meth)acrylate, since distribution of lactone continuous chains becomes broad and the number (n) of continuous chain length becomes large, although a curing reactivity and flexibility are improved, there is occasionally caused

a problem of a decline of hardness and acid resistance.

On the other hand, as radically polymerizable unsaturated monomers having carboxylic group, there are known (meth)acrylic acid, itaconic acid, maleic acid, β -(meth)acryloyloxyethyl succinic acid, β -(meth)acryloyloxyethyl maleic acid, and β -(meth)acryloyloxyethyl phthalic acid, etc.

The radically polymerizable unsaturated monomers having carboxylic group are employed in exceedingly wide range uses as a raw material and an intermediate for a thermosetting coating, an adhesive, an modifier for processing papers, a crosslinking agent, and a processing agent for fibers, etc., it is required that a kind of the radically polymerizable unsaturated monomers is carefully selected like being appropriate for respective uses.

Generally speaking, as a method for synthesizing a polyester unsaturated monomer having carboxylic group at a terminal, there are known a method in which an ω -hydroxycarboxylic acid is allowed to react with a radically polymerizable unsaturated monomers having carboxylic group, a method in which an α, ω -polyester dicarboxylic acid is allowed to react with a radically polymerizable unsaturated monomers having hydroxyl group, and a method, etc. in which an acid anhydride is allowed to react with a radically polymerizable unsaturated monomers having carboxylic group and an epoxy compound.

However, the methods include a problem that there are largely produced products quite not having a radically polymerizable functional group or products having two radically polymerizable functional group as by-products.

Further, as another method, there is a method in which a metal

salt of a radically polymerizable unsaturated monomers having carboxylic group, for example, sodium acrylate is allowed to react with an ω -halogenocarboxylic acid, for example, ϵ -chlorocaproic acid.

However, in the methods, an ω -halogenocarboxylic acid which is a raw material is prepared through many steps for the preparation, and a plurality of steps are required for introducing two or more pieces of a radically polymerizable functional groups and, further, there is also required a step for separating a halogenated metal salt by-produced, as a result, an industrial preparation method is not still actualized.

As a method for intending to improve such the drawbacks, for example, JP-A-60067446 proposes a method. In the method, a radically polymerizable unsaturated monomers having carboxylic group is allowed to react with ϵ -caprolactone under the presence of an acidic catalyst to prepare a caprolactone polyester unsaturated monomer, and a fair result is obtained as an industrial method for the preparation. However, an acrylic resin prepared using the monomer often shows tackiness, and it includes a problem as an electric material.

Purpose of the present invention I is to provide a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactone which is employed as an industrial finishing agent (a coating) having a high quality and which is well-balanced in a variety of physical properties in a coating layer, for example, through using as a comonomer in a polymerization reaction with other monomers, and to provide an acrylic polyol resin using the composition.

Purpose of the present invention II is to provide a method for the preparation of the composition.

Purpose of the present invention III is to provide a curable type coating composition in which an acid resistance is elevated even though in a melamine type which is low in price, and which is well-balanced in abrasion resistance and the acid resistance.

Purpose of the present invention IV is to provide a melamine-curable type water-based coating composition which is excellent in hardness, water resistance, restoring resistance, and processability, etc. of a coating layer, and which is excellent for cars, home electric appliances, and cans for beverages and foods.

Purpose of the present invention V is to provide an isocyanate system curable type coating composition which has a sufficient pot-life and, in which a problem of abrasion resistance is solved while maintaining an excellent acid resistance, adhesion, water resistance, and hardness.

Purpose of the present invention VI is to provide an isocyanate system curable type coating composition which has a sufficient pot-life and, in which a problem of abrasion resistance is solved while maintaining excellent acid resistance, adhesion, water resistance, and hardness.

Purpose of the present invention VII is to provide a thermosetting resin composition in which a problem of the above-described acid resistance and odor is solved which are important in a coating for cars, and in which hardness and abrasion resistance, water resistance, and solvent resistance are improved by elevating a crosslinking density, and to provide a top-coat clear coating using the composition.

Purpose of the present invention VIII is to provide an industrially-feasible method for the preparation of a carboxylic group-contained acrylate composition modified by a small amount of lactones.

Purpose of the present invention IX is to provide a high solid curable resin composition in which the above-described problems are solved and, which is capable of forming a thin layer which is excellent in acid resistance to an acid rain, abrasion resistance, yellowing resistance, and outer appearance, and to provide a method for coating (hereinafter, also occasionally referred to as a method for forming a coating layer) using the composition.

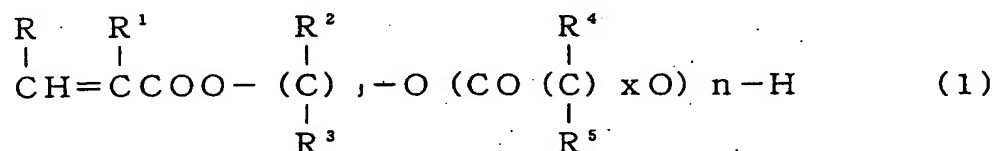
Purpose of the present invention X is to provide a polyester unsaturated monomer composition modified by a small amount of lactone which is obtained through an addition reaction of lactone by decreasing lactone chains, which is employed as an industrial finishing agent (a coating) having a high quality which is well-balanced in various physical properties of a coating layer by employing as a comonomer in a polymerization reaction with other monomers, and to provide a method for the preparation thereof, and to provide an acrylic resin using thereof which does not show tackiness so much.

DISCLOSURE OF THE INVENTION

The present inventor, as a result of an intensive investigation for attaining the purpose of the present invention I, found out that the above-described requirements can be satisfied by a hydroxyalkyl(meth)acrylate composition in which there is decreased a proportion of monomers containing two or more continuous chains (n

≥ 2) of lactones by allowing to react in a large reaction ratio (the former mol number/the latter mol number) of a hydroxyalkyl(meth)acrylate with respect to a lactone monomer, and the present invention has been completed.

That is, No. 1 in the present invention I provides a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones, in which a proportion of monomers having two or more continuous chains ($n \geq 2$) of lactones is less than 50% (area % by GPC) which is represented by general formula (1) described below,



(in the formula, R, R¹, R², and R³ are independently a hydrogen or a methyl group, j is an integer of 2-6, xn pieces of R⁴ and R⁵ are independently a hydrogen or an alkyl group having a carbon number of 1-12, "x" is 4-7, "n" is 0 or an integer of not less than 1, and an average value of "n" in the composition is not less than 0.3 to less than 1.0).

Further, No. 2 in the present invention I provides a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones as described in No. 1 of the present invention I, in which the hydroxyalkyl(meth)acrylate is a hydroxyethyl(meth)acrylate.

Still further, No. 3 in the present invention I provides a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones as described in No. 1 of the present invention I, in which

the lactone monomer which is employed as a raw material is ϵ -caprolactone and/or valerolactone.

Furthermore, No. 4 in the present invention I provides a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones as described in No. 1 of the present invention I, in which the content of the lactone monomer remained in the composition is 0-10% by weight.

Besides, No. 5 in the present invention I provides a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones as described in No. 1 of the present invention I in which the content of the hydroxyalkyl(meth)acrylate remained in the composition is not less than 20% by weight and not more than 50% by weight.

Also, No. 6 in the present invention I provides a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones as described in No. 1 of the present invention I, in which the content of a di(meth)acrylate which is a by-product in the composition is not more than 2% by weight.

And also, No. 7 in the present invention I provides a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones as described in No. 1 of the present invention I, in which the content of by-products is not more than 10% by weight in the composition, which are produced by side reactions such as a Michaels addition, an acrylic polymerization, a transesterification, and other side reactions.

And also, No. 8 in the present invention I provides a hydroxyalkyl(meth)acrylate composition modified by a small amount of

lactones as described in any one of Nos. 1-7 of the present invention I, in which the amount of a catalyst to be employed in the ring-opening polymerization for the preparation of the composition is less than 1000 ppm (by weight) based on total amount of materials to be fed.

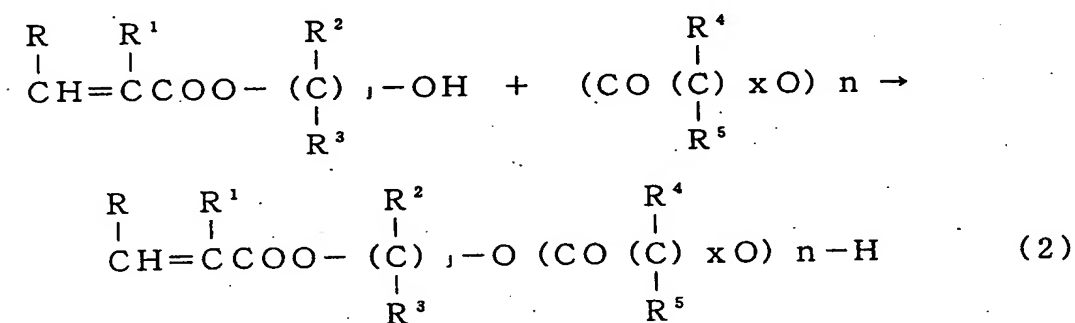
Also, No. 9 in the present invention I provides a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones as described in any one of Nos. 1-8 of the present invention I, in which a polymerization inhibitor is not more than 1% by weight based on total amount, which is employed for the hydroxyalkyl(meth)acrylate in the ring-opening polymerization for the preparation of the composition.

And also, No. 10 in the present invention I provides an acrylic polyol resin which is obtained using a hydroxyalkyl (meth)acrylate composition modified by a small amount of lactones as described in any one of Nos. 1-9 of the present invention I as a component for polymerization.

The present inventor, as a result of an intensive investigation for attaining the purpose of the present invention II, found out that there can be obtained a lactone-modified hydroxyalkyl(meth)acrylate composition in which lactone continuous chains are decreased by allowing to react a hydroxyalkyl(meth)acrylate with a lactone in a reaction molar ratio of more than 1 (mol number of the former/mol number of the latter), and the present invention has been completed.

That is, No. 1 in the present invention II provides a method for the preparation of a lactone-modified hydroxyalkyl (meth)acrylate composition in which a proportion of monomers having not less than 2 continuous chains ($n \geq 2$) of lactones is less than 50% by mol (GPC

area %), characterized in that a hydroxyalkyl (meth)acrylate is allowed to react with a lactone in a reaction molar ratio of more than 1 in the case of preparing the polylactone-modified hydroxyalkyl(meth)acrylate through allowing to react the hydroxyalkyl(meth)acrylate with a lactone monomer by ring-opening polymerization according to a reaction represented by a general formula (2) described below.



(in the formula, R, R¹, R², and R³ are independently a hydrogen or a methyl group, "j" is an integer of 2-6, xn pieces of R⁴ and R⁵ are independently a hydrogen or an alkyl group having a carbon number of 1-12, "x" is 4-7, "n" is 0 or an integer of not less than 1, and an average value of "n" in the composition is not less than 0.3 to less than 1.0).

Further, No. 2 in the present invention II provides a method for the preparation of a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones as described in No. 1 of the present invention II, in which the hydroxyalkyl(meth)acrylate is hydroxyethylacrylate or hydroxyethylmethacrylate.

Still further, No. 3 in the present invention II provides a method for the preparation of a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones as described in No. 1 or 2 of

the present invention II, in which the lactone monomer is ϵ -caprolactone and/or valerolactone.

Furthermore, No. 4 in the present invention II provides a method for the preparation of a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones as described in any one of Nos. 1-3 of the present invention II in which an average value of n is not less than 0.35 and not more than 1.0.

Besides, No. 5 in the present invention II provides a method for the preparation of a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones as described in any one of Nos. 1-3 of the present invention II, in which the content of the lactone monomer remained in the composition is 0-10% by weight.

Also, No. 6 in the present invention II provides a method for the preparation of a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones as described in any one of Nos. 1-3 of the present invention II in which the content of the hydroxyalkyl(meth)acrylate remained in the composition is not less than 20% by weight and not more than 50% by weight.

And also, No. 7 in the present invention II provides a method for the preparation of a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones as described in any one of Nos. 1-3 of the present invention II, in which the content of a di(meth)acrylate which is a by-product in the composition is not more than 2% by weight.

And also, No. 8 in the present invention II provides a method for the preparation of a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones as described in any one of Nos.

1-3 of the present invention II, in which the content of by-products is not more than 10% by weight in the composition, which are produced by side reactions such as a Michaels addition, an acrylic polymerization, a transesterification, and other side reactions.

And also, No. 9 in the present invention II provides a method for the preparation of a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones as described in any one of Nos. 1-8 of the present invention II, in which the amount of a catalyst to be employed in the reaction of the lactone with the hydroxyalkyl(meth)acrylate is less than 1000 ppm (by weight) based on total amount of materials to be fed.

And also, No. 10 in the present invention II provides a method for the preparation of a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones as described in any one of Nos. 1-9 of the present invention II, in which the content of an inhibitor in polymerization of the hydroxyalkyl(meth)acrylate with the lactones is not more than 1% by weight based on total amount of materials to be fed.

The present inventor, as a result of an intensive investigation for attaining the purpose of the present invention III, found out that the above-described requirement can be satisfied by a curable resin composition containing 0.5-80 parts by weight of an acrylic polyol resin (A) obtained using a hydroxyalkyl(meth)acrylate composition (a) in which a proportion of monomers having not less than 2 continuous chains ($n \geq 2$) of lactones is decreased and 0.5-50 parts by weight of a melamine resin (III-B) as essential components, and the present

invention has been completed.

That is, No. 1 in the present invention III provides a curable resin composition containing 0.5-80 parts by weight of an acrylic polyol resin (A) obtained using a hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones in which a proportion of monomers having not less than 2 continuous chains ($n \geq 2$) of lactones is less than 50% (GPC area %) as polymerizing components and 0.5-50 parts by weight of a melamine resin (B) [total of the (A) and (B) does not exceed 100 parts by weight].

Further, No. 2 in the present invention III provides a curable resin composition as described in No. 1 of the present invention III, in which the hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones is obtained using a hydroxyethyl(meth)acrylate.

Still further, No. 3 in the present invention III provides a curable resin composition as described in No. 1 or 2 of the present invention III, in which the hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones is obtained using ϵ -caprolactone, δ -valerolactone, γ -butyrolactone, or a mixture thereof as lactone monomers.

Besides, No. 4 in the present invention III provides a curable resin composition as described in any one of Nos. 1-3 of the present invention III, in which the acrylic polyol resin (A) is composed of 5-70 parts by weight of the hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones, 0-90 parts by weight of an alkyl(meth)acrylate having a carbon number of 1-20, 0-30 parts by

weight of a (meth)acrylic acid, and 0-40 parts by weight of other polymerizable unsaturated monomer.

Also, No. 5 in the present invention III provides a curable resin composition as described in any one of Nos. 1-4 of the present invention III, in which the acrylic polyol resin (A) has a hydroxyl group value of 5-250 and a number average molecular weight of 3,000-300,000.

The present inventor, as a result of an intensive investigation for attaining the purpose of the present invention IV, found out that the above-described problems can be solved by using a melamine-curable type water-based coating composition composed of an acrylic polyol resin (A) obtained by a specified hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones and an amino-plasto resin (B), and the present invention has been completed.

That is, No. 1 in the present invention IV provides a melamine-curable type water-based coating composition containing 5-30 parts by weight of an acrylic polyol resin (A) obtained using a hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones represented by the above-described general formula (1), in which a proportion of monomers having not less than 2 continuous chains ($n \geq 2$) of lactones is less than 50% (GPC area %) as polymerizing components and 10-60 parts by weight of an amino-plasto resin (IV-B).

No. 2 in the present invention IV provides a melamine-curable type water-based coating composition as described in No. 1 of the present invention IV, characterized in that the acrylic polyol resin (A) is composed of (i) 3-40% by weight of the hydroxyalkyl (meth)acrylate

composition (a) modified by a small amount of lactones, (ii) 1-20% by weight of α, β -unsaturated carboxylic acid, (iii) 1-25% by weight of an N-alkoxymethyl(meth)acrylate having a carbon number of 1-6 in an alkyl group, and (iv) an aromatic vinyl monomer and an alkyl(meth)acrylate which are contained in an amount that 100% by weight minus the total weight of the above components (i), (ii), and (iii).

No. 3 in the present invention IV provides a melamine-curable type water-based coating composition as described in No. 1 or 2 of the present invention IV, in which the acrylic polyol resin (A) has a number average molecular weight of 2,000-50,000, a hydroxyl group value of 10-150, and a Tg point of 0-60°C.

No. 4 in the present invention IV provides a melamine-curable type water-based coating composition as described in any one of Nos. 1-3 of the present invention IV, in which the amino-plasto resin (IV-B) is at least one of a melamine resin (j), a guanamine resin (k) selected from benzoguanamine, spiroguanamine, acetoguanamine, and phthaloguanamine, and/or a melamine-guanamine cocondensed resin (l).

No. 5 in the present invention IV provides a melamine-curable type water-based coating composition as described in any one of Nos. 1-4 of the present invention IV, which is employed for cars, home electric appliances, and cans for beverages and foods.

The present inventors, as a result of an intensive investigation for attaining the purpose of the present invention V, found out that the above-described requirement can be satisfied by a curable resin composition essentially containing 50-90 parts by weight of an acrylic polyol resin (A) obtained using a hydroxyalkyl(meth)acrylate

composition (a) in which a proportion of monomers having not less than 2 continuous chains ($n \geq 2$) of lactones is reduced and which is obtained by a large reaction molar ratio of a hydroxyalkyl(meth)acrylate with lactone monomers (the former mol number/the latter mol number), and 10-50 parts by weight of a polyisocyanate compound (V-B), and the present invention has been completed.

That is, No. 1 in the present invention V provides a curable resin composition containing 50-90 parts by weight of an acrylic polyol resin (V-A) obtained using a hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones which is represented by the above-described general formula (1) in which a proportion of monomers having not less than 2 continuous chains ($n \geq 2$) of lactones is less than 50% (GPC area %) as polymerizing components and 50-10 parts by weight of a polyisocyanate compound (V-B) [total of the (V-A) and (V-B) does not exceed 100 parts by weight].

No. 2 in the present invention V provides a curable resin composition as described in No. 1 of the present invention V, in which the acrylic polyol resin (V-A) is composed of 5-65% by weight of the hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones, 0-30% by weight of a vinyl monomer having hydroxyl group, 0.1-20% by weight of a polyester resin having a copolymerizable unsaturated group, and other vinyl monomers (residual weight).

The present inventor, as a result of an intensive investigation for attaining the purpose of the present invention VI, found out that the above-described requirement can be satisfied by a curable resin

composition essentially containing 0.5-80 parts by weight of an acrylic polyol resin (A) obtained using a hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones, and which is obtained by a large reaction molar ratio of a hydroxyalkyl(meth)acrylate with lactone monomers (the former mol number/the latter mol number), and in which a proportion of monomers having not less than 2 continuous chains ($n \geq 2$) of lactones is reduced, and 0.5-50 parts by weight of a polyisocyanate compound (C), and the present invention has been completed.

That is, No. 1 in the present invention VI provides a curable resin composition containing 0.5-80 parts by weight of an acrylic polyol resin (VI-A) having carboxylic group and a functional group obtained by allowing to react a hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones represented by the general formula (1) described in claim 1 in which a proportion of monomers having not less than 2 continuous chains ($n \geq 2$) of lactones is less than 50% (GPC area %) with a vinyl monomer having carboxylic group and other vinyl monomers, and 0.5-50 parts by weight of a polyisocyanate compound (VI-B) [total of the (VI-A) and (VI-B) does not exceed 100 parts by weight] as essential components.

Further, No. 2 of the present invention VI provides a curable resin composition as described in No. 1 of the present invention VI, in which the acrylic polyol resin (VI-A) is a vinyl copolymer having carboxylic group and a functional group obtained by allowing to react a reaction product of a hydroxyl group-contained resin obtained by copolymerizing a hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones with a (meth)acrylic anhydride, and then,

by allowing to react the reaction product with a vinyl-based monomer having carboxylic group and other vinyl-based monomers.

Still further, No. 3 of the present invention VI provides a curable resin composition as described in No. 2 of the present invention VI, in which the acrylic polyol resin (VI-A) is a resin obtained using the hydroxyl group-contained resin in the No. 2 of the present invention VI and at least one selected from a urethane resin having hydroxyl groups, an epoxy resin having hydroxyl groups, a cellulose derivative having hydroxyl groups, and a polyester resin having hydroxyl groups as the resin having hydroxyl groups.

Furthermore, No. 4 of the present invention VI provides a curable resin composition as described in No. 2 of the present invention VI, in which the acrylic polyol resin (VI-A) is a resin obtained using the hydroxyl group-contained resin in the No. 2 of the present invention VI and a urethane resin having hydroxyl groups as the resin having hydroxyl groups.

Besides, No. 5 in the present invention VI provides a curable resin composition as described in any one of Nos. 1-4 of the present invention VI, in which the polyisocyanate compound (VI-B) is a polyisocyanate compound containing an epoxy resin.

Also, No. 6 in the present invention VI provides a curable resin composition as described in any one of Nos. 1-5 of the present invention VI, in which the hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones is a product obtained using hydroxyethyl(meth)acrylate.

And also, No. 7 of the present invention VI is a coating characterized by containing (i) crosslinked particles obtained by

dispersing a mixture of the acrylic polyol resin (VI-A) with the polyisocyanate compound (VI-B) into a water-based medium and by crosslinking thereof, or (ii) composite-type crosslinked particles composed of a urethane-urea/ethylene-based resin obtained through polymerizing polymerizable ethylene-based unsaturated compounds containing the hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones in water in which crosslinked urethane-urea particles are dispersed, as resin components for forming a thin layer.

And also, No. 8 of the present invention VI is a coating as described in No. 7 of the present invention VI characterized by containing more than 50% by weight of crosslinked particles having particle diameter of not more than 1 μ m and, moreover, an average molecular weight between crosslinking points of a range of 300-2,000, as resin components for forming a thin layer.

And also, No. 9 of the present invention VI is a coating as described in No. 7 or 8 of the present invention VI, in which the crosslinked particles have a thin layer-formable temperature of not more than 100°C.

And also, No. 10 of the present invention VI is a coating as described in any one of Nos. 7-9 of the present invention VI, in which the content of the crosslinked particles is not less than 70% in the resin components for forming a thin layer.

And also, No. 11 of the present invention VI is a coating as described in any one of Nos. 7-10 of the present invention VI, characterized by containing 1-25% by weight of a crosslinking agent together with the crosslinked particles as the resin components for forming a thin layer.

And also, No. 12 of the present invention VI is a coating as

described in any one of Nos. 7-11 of the present invention VI, characterized by further containing a thin layer-formable resin having a reactive group other than the crosslinked particles as the resin components for forming a thin layer.

And also, No. 13 of the present invention VI is a coating as described in any one of Nos. 7-12 of the present invention VI, in which the crosslinked particles contain pigments in an inside thereof.

The present inventor, as a result of an intensive investigation for attaining the purpose of the present invention VI, found out that the problems can be solved by using a curable resin composition which comprises an acrylic polyol resin (VII-A) having hydroxyl groups composed of a hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones which has hydroxyl group at a terminal, and an acrylic copolymer (VII-B) having an alkoxysilyl group, and the present invention has been completed.

That is, No. 1 in the present invention VII provides a thermosetting resin composition which contains at least 2-50 parts by weight of an acrylic polyol resin (VII-A) containing a hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones represented by the general formula (1) in which a proportion of monomers having not less than 2 continuous chains ($n \geq 2$) of lactones is less than 50% (GPC area %) as a polymerizable component, and 30-80 parts by weight of an acrylic copolymer (VII-B) having an alkoxysilyl group [total of the (VII-A) and (VII-B) does not exceed 100 parts by weight], as polymerizable components.

No. 2 of the present invention VII provides a thermosetting resin composition as described in No. 1 of the present invention VII, in which the acrylic polyol resin (VII-A) further has at least one kind selected from an acid anhydride group, an epoxy group, amino group, and carboxylic group.

No. 3 of the present invention VII provides a thermosetting resin composition as described in No. 1 or 2 of the present invention VII, in which the acrylic copolymer (VII-B) having an alkoxysilyl group has a group represented by general formula (VII-3) described below,



(in the formula, R^6 represents an alkyl group having a carbon number of 1-10, R^7 and R^8 are a hydrogen atom or a monovalent hydrocarbon group selected from an alkyl group, an aryl group, and an aralkyl group which have a carbon number of 1-10, "a" is the number of a substituted group, and it represents an integer of 0, 1, or 2).

No. 4 of the present invention VII provides a thermosetting resin composition as described in No. 3 of the present invention VII, in which the acrylic copolymer (VII-B) having an alkoxysilyl group further has at least one kind selected from an acid anhydride group, an epoxy group, amino group, and carboxylic group.

No. 5 of the present invention VII provides a thermosetting resin composition as described in No. 3 or 4 of the present invention VII, in which the acrylic copolymer (VII-B) having an alkoxysilyl group has a number average molecular weight of 1,000-30,000.

No. 6 of the present invention VII provides a thermosetting resin

composition as described in any one of Nos. 3-5 of the present invention VII, in which the acrylic copolymer (VII-B) having an alkoxysilyl group contains 5-90% by weight of an alkoxysilyl group-contained monomer (VII-b) having a polymerizable unsaturated double bond as a polymerizing component.

No. 7 of the present invention VII provides a thermosetting resin composition containing 0.1-20 parts by weight of a catalyst (VII-C) for curing based on 100 parts by weight of the thermosetting resin composition as described in any one of Nos. 1-6 of the present invention VII.

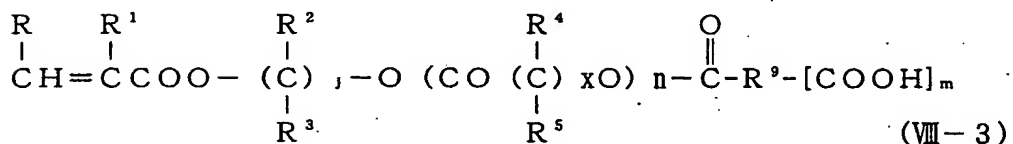
No. 8 of the present invention VII provides a thermosetting resin composition as described in No. 7 of the present invention VII, in which the catalyst (VII-C) for curing is an organic tin compound, an acidic phosphate, a mixture or a reaction product of the acidic phosphate with an amine, a saturated or unsaturated polycarboxylic acid, a saturated or unsaturated polycarboxylic anhydride, a reactive silicone compound, an organic titanate compound, an organic aluminum compound, or a mixture thereof.

No. 9 of the present invention VII provides a top coat clear coating essentially containing a thermosetting resin composition as described in Nos. 1-8 of the present invention VII.

The present inventor, as a result of an intensive investigation for attaining the purpose of the present invention VIII, found out that there can be industrially and advantageously prepared a carboxylic group-contained acrylate monomer modified by small amount of lactones by allowing to react a hydroxyalkyl (meth)acrylate composition modified

by a small amount of lactones which has hydroxyl group at a terminal with a carboxylic acid or an anhydride thereof, and the present invention has been completed.

That is, No. 1 of the present invention VIII provides a method for the preparation of a carboxylic group-contained acrylate composition (a') modified by a small amount of lactones represented by a general formula (VIII-3) described below by allowing to react the hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones represented by the above-described general formula (1) in which a proportion of monomers having not less than 2 continuous chains ($n \geq 2$) of lactones is less than 50% (GPC area %) with a carboxylic acid or anhydride (VIII-b) thereof represented by a general formula (VIII-2) described below,



(in the formula, R, R¹, R², and R³ are independently a hydrogen or a methyl group, "j" is an integer of 2-6, xn pieces of R⁴ and R⁵ are independently a hydrogen atom or an alkyl group having a carbon number of 1-12, "x" is 4-7, "n" is 0 or an integer of not less than 1, an average value of "n" in the composition is not less than 0.3 to less than 1.0, R⁹ is a residual group of a carboxylic acid, and "m" is an integer of 1-3).

No. 2 of the present invention VIII provides a method for the preparation of a carboxylic group-contained acrylate composition (a')

modified by a small amount of lactones as described in No. 1 of the present invention VIII, characterized in that a reaction of the hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones with the carboxylic acid or anhydride (VIII-b) thereof is conducted at a range of 40-160°C.

No. 3 of the present invention VIII provides a method for the preparation of a carboxylic group-contained acrylate composition (a') modified by a small amount of lactones as described in No. 1 or 2 of the present invention VIII, characterized in that a reaction of the hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones with the carboxylic acid or anhydride thereof (VIII-b) is conducted under the presence of oxygen and a polymerization inhibitor.

No. 4 of the present invention VIII provides a method for the preparation of a carboxylic group-contained acrylate composition (a') modified by a small amount of lactones as described in any one of Nos. 1-3 of the present invention VIII, characterized in that 0.9-1.1 mol of the carboxylic acid or anhydride (VIII-b) thereof is allowed to react with 1 mol of the hydroxy(meth)acrylate composition (a) modified by a small amount of lactones.

The present inventor found out that the purpose of the present invention IX can be attained by using a resin composition comprising an acrylic polycarboxylic acid resin (A') containing a carboxylic group-contained acrylate composition (a') modified by a small amount of lactones as a polymerizing component and a polyoxide (IX-B), and the present invention has been completed.

That is, No. 1 of the present invention IX provides a curable resin composition comprising 10-70 parts by weight of an acrylic polycarboxylic acid resin (A') containing the carboxylic group-contained acrylate composition (a') modified by a small amount of lactones represented by the above-described general formula (VIII-3) in which a proportion of monomers having not less than 2 continuous chains ($n \geq 2$) of lactones is less than 50% (GPC area %) as a polymerizing component and 10-80 parts by weight of a polyepoxide (IX-B).

No. 2 of the present invention IX provides a curable resin composition as described in No. 1 of the present invention IX, characterized in that the carboxylic group-contained hydroxy(meth)acrylate composition (a') modified by a small amount of lactones is obtained by allowing to react the hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones represented by the above-described general formula (1) in which a proportion of monomers having not less than 2 continuous chains ($n \geq 2$) of lactones is less than 50% (GPC area %) with the carboxylic acid or the anhydride thereof represented by the above-described general formula (VIII-2).

No. 3 of the present invention IX provides a curable resin composition as described in No. 2 of the present invention IX, characterized in that the carboxylic group-contained hydroxy(meth)acrylate composition (a') modified by a small amount of lactones is obtained by allowing to react 0.9-1.1 mol of the carboxylic acid or the anhydride thereof with respect to 1 mol of the hydroxy(meth)acrylate composition (a) modified by a small amount of

lactones.

No. 4 of the present invention IX provides a curable resin composition as described in any one of Nos. 1-3 of the present invention IX, characterized in that the acrylic polycarboxylic acid resin (A') is a copolymer of 5-80% by weight of a carboxylic group-contained ethylenic unsaturated monomer with 20-95% by weight of an ethylenic unsaturated monomer not having carboxylic group, provided that the ratio of the carboxylic group-contained hydroxy(meth)acrylate composition (a') modified by a small amount of lactones is 5-50% by weight in the acrylic polycarboxylic acid resin (A'), and the copolymer has at least two carboxylic groups on average in the molecule and an acid value of 5-300 mgKOH/g-solid and a number average molecular weight of 500-8000.

No. 5 of the present invention IX provides a curable resin composition as described in any one of Nos. 1-4 of the present invention IX, characterized in that terminal carboxylic groups in the acrylic polycarboxylic acid resin (A') are an acrylic polycarboxylic acid resin (bA') blocked by a blocking group which can discharge carboxylic groups by heat and/or water.

No. 6 of the present invention IX provides a curable resin composition as described in any one of Nos. 1-5 of the present invention IX, characterized in that the polyepoxide (IX-B) is an acrylic polyepoxide having an epoxy equivalent of 50-700 and a number average molecular weight of 200-10000.

No. 7 of the present invention IX provides a curable resin composition as described in any one of Nos. 1-6 of the present invention IX, characterized in that the polyepoxide (IX-B) is a polyepoxide having

hydroxyl group and an epoxy group which is obtained by copolymerization of 5-70% by weight of (i) a hydroxyl group-contained ethylenic unsaturated monomer having a structure represented by a formula (4) described below with 10-60% by weight of (ii) an epoxy group-contained ethylenic unsaturated monomer and optionally 0-85% by weight of (iii) an ethylenic unsaturated monomer not having an epoxy group,

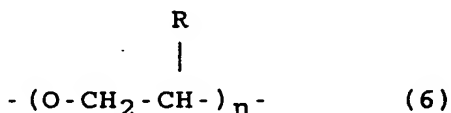


[in the formula, R is a hydrogen atom or a methyl group, and X is an organic chain shown by formula (5) described below,



(in the formula, Y is a linear or branched alkylene group having a carbon number of 2-8, "m" is an integer of 3-7, and "q" is an integer of 0-4),

or an organic chain shown by formula (6) described below,



(in the formula, R is a hydrogen atom or a methyl group, and n is an integer of 2-50)].

No. 8 of the present invention IX provides a curable resin composition as described in any one of Nos. 1-7 of the present invention IX, and which further contains 0.1-10 parts by weight of an antioxidant (IX-C).

No. 9 of the present invention IX provides a curable resin composition as described in any one of Nos. 1-8 of the present invention IX, and which further contains 5-70 parts by weight of a polyester polycarboxylic acid (IX-D) having an acid value of 30-350

mg-KOH/g-solid.

No. 10 of the present invention IX provides a curable resin composition as described in any one of Nos. 1-9 of the present invention IX, and which further contains 0.1-10 parts by weight of crosslinked resin particles (IX-E).

No. 11 of the present invention IX provides a clear coating composition containing a curable resin composition as described in any one of Nos. 1-10 of the present invention IX as a binder.

No. 12 of the present invention IX provides a method for coating which includes a step in which a water-based or a solvent-based base coating is coated on a substrate coated by under-coating or internally-coating; a step in which a clear coating composition of No. 1 in the present invention IX is coated on the base coating layer without curing; and a step in which a layer of the base coating and a layer of the clear coating are cured by heating.

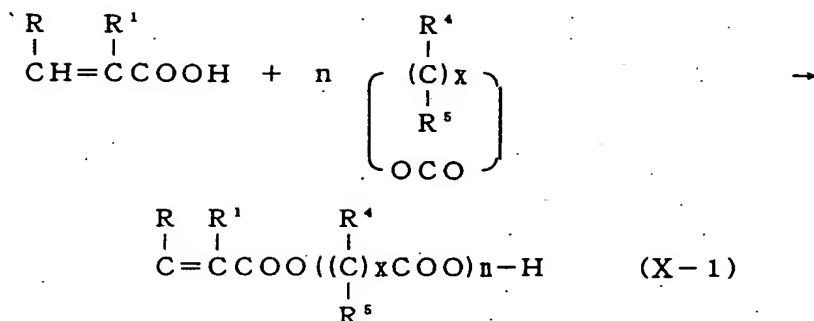
In the above descriptions, part is part by weight.

The present inventor, as a result of an intensive investigation for attaining the purpose of the present invention X, found out that the above-described requirement can be satisfied by a polyester unsaturated monomer composition modified by a small amount of lactones, in which a proportion of monomers having not less than 2 continuous chains ($n \geq 2$) of lactones is decreased by a large reaction molar ratio (the former mol number/the latter mol number) of a carboxylic group-contained polymerizable unsaturated monomer, and the present invention has been completed.

That is, No. 1 of the present invention X provides a polyester unsaturated monomer composition modified by a small amount of lactones, in which a proportion of monomers having not less than 2 continuous chains ($n \geq 2$) of lactones is less than 50% (GPC area %) with respect to total of polymerizable unsaturated monomers containing carboxylic group, and which are obtained by a ring-opening polymerization of a lactone monomer.

No. 2 of the present invention X provides a polyester unsaturated monomer composition modified by a small amount of lactones as described in No. 1 of the present invention X, in which the polymerizable unsaturated monomers containing carboxylic group are at least one kind selected from a group consisting of a (meth)acrylic acid, itaconic acid, β -(meth)acryloyloxyethyl succinic acid, β -(meth)acryloyloxyethyl maleic acid, β -(meth)acryloyloxyethyl phthalic acid, maleic acid, a monoalkyl maleate (a carbon number in an alkyl group is 1-12), tetrahydrophthalic acid, and an anhydride thereof.

No. 3 of the present invention X provides a polyester unsaturated monomer composition modified by a small amount of lactones as described in No. 2 of the present invention X, in which the polymerizable unsaturated monomers containing carboxylic group are a (meth)acrylic acid, and which is obtained by a reaction represented by formula (11) described below,



(in the formula, R and R¹ are independently a hydrogen atom or a methyl group, xn pieces of R⁴ and R⁵ are independently a hydrogen atom or an alkyl group having a carbon number of 1-12, "x" is 4-7, "n" and "n" in the composition are 0 or an integer of not less than 1, and an average value of "n" in the composition is not less than 0.3 to less than 1.0).

No. 4 of the present invention X provides a polyester unsaturated monomer composition modified by a small amount of lactones as described in any one of Nos. 1-3 of the present invention X, in which the lactone monomer is a lactone having 5, 6, 7 and/or 8-members ring.

No. 5 of the present invention X provides a polyester unsaturated monomer composition modified by a small amount of lactones as described in any one of Nos. 1-4 of the present invention X, in which the lactone monomer is ϵ -caprolactone and/or valerolactone.

No. 6 of the present invention X provides a polyester unsaturated monomer composition modified by a small amount of lactones as described in any one of Nos. 1-5 of the present invention X, characterized in that the proportion of monomers having not less than 2 continuous chains ($n \geq 2$) of lactones is less than 40% (GPC area %).

No. 7 in the present invention I provides a polyester unsaturated monomer composition modified by a small amount of lactones as described

in any one of Nos. 1-6 of the present invention X, in which the content of residual lactone monomers is 0-10% by weight.

No. 8 in the present invention X provides a polyester unsaturated monomer composition modified by a small amount of lactones as described in any one of Nos. 1-7 of the present invention X, in which the content of the residual polymerizable unsaturated monomers containing carboxylic group is more than 20% by weight and not more than 50% by weight.

No. 9 in the present invention X provides a polyester unsaturated monomer composition modified by a small amount of lactones as described in any one of Nos. 1-8 of the present invention X, in which the content of a di(meth)acrylate of the polymerizable unsaturated monomers containing carboxylic group which is a by-product is not more than 2% by weight.

No. 10 in the present invention X provides a polyester unsaturated monomer composition modified by a small amount of lactone as described in any one of Nos. 1-9 of the present invention X, in which the content of by-products produced by side reactions such as a Michaels addition, an acrylic polymerization, a transesterification, and other side reactions is not more than 10% by weight.

No. 11 in the present invention X provides a polyester unsaturated monomer composition modified by a small amount of lactone as described in any one of Nos. 1-10 of the present invention X, in which the amount of a catalyst to be employed in the ring-opening polymerization is less than 1000 ppm by weight based on total amount of materials to be fed.

No. 12 in the present invention X provides a polyester unsaturated

monomer composition modified by a small amount of lactone as described in any one of Nos. 1-11 of the present invention X, in which a polymerization inhibitor is not more than 1% by weight based on total amount to be fed, which is employed for a (meth)acrylic acid in the ring-opening polymerization.

No. 13 in the present invention X provides a method for the preparation of a polyester unsaturated monomer composition modified by a small amount of lactone, in which 0.3-less than 1.0 mol of a lactone monomer is polymerized by ring-opening with respect to 1 mol of a radically polymerizable unsaturated monomers containing carboxylic group, and a proportion of monomers having not less than 2 continuous chains ($n \geq 2$) of lactones is adjusted to less than 50%.

No. 14 in the present invention X provides a method for the preparation of a polyester unsaturated monomer composition modified by a small amount of lactone as described in No. 13 of the present invention X, in which an acidic catalyst is a Lewis acid or a Br nsted acid.

No. 15 in the present invention X provides an acrylic resin using a polyester unsaturated monomer composition modified by a small amount of lactone as described in any one of Nos. 1-12 of the present invention X.

No. 16 in the present invention X is a method for the preparation of a polyester unsaturated monomer composition modified by a small amount of lactone, characterized in that 0.3-less than 1.0 mol of a lactone monomer is polymerized by ring-opening with respect to 1 mol of a radically polymerizable unsaturated monomers containing carboxylic group using a stannous halide, monobutyltin

tris-2-ethylhexanate, stannous octoate, dibutyltin dilaurate, or a mixture thereof as a catalyst, followed by separating unreacted radically polymerizable unsaturated monomers containing carboxylic group.

No. 17 in the present invention X is a method for the preparation of a polyester unsaturated monomer composition modified by a small amount of lactone as described in claim 85, in which the catalyst to be employed in the ring-opening polymerization is less than 1000 ppm by weight based on total amount of materials to be fed.

By the present invention, there can be prepared a polyester unsaturated monomer modified by a small amount of lactone having the same number of a radically polymerizable functional group as in the radically polymerizable unsaturated monomer having carboxylic group which is employed as a raw material, and in which an average addition amount of lactones is 0.35 to not more than 1.0 mol.

Particularly, in the case that there are employed, for example, acrylic acid and methacrylic acid as the radically polymerizable unsaturated monomer having carboxylic group, there can be prepared the polyester unsaturated monomer modified by a small amount of lactone which essentially contains 1 piece of a radically polymerizable functional group without producing a compound not having a radically polymerizable functional group at all and a compound having two or more pieces of a radically polymerizable functional group.

The polyester unsaturated monomer modified by a small amount of lactone obtained has a reactive carboxylic group at one terminal thereof and, further, it has a feature that there is a radically polymerizable unsaturated group at a position which exists far apart from the

carboxylic group.

Further, in the acrylic resin composition using the polyester unsaturated monomer modified by a small amount of lactone of the present invention, since tackiness can be removed by elevating Tg of the resin composition, it is particularly useful in an electric material field, etc.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 shows an example of a continuous chain distribution of ϵ -caprolactone obtained from a gel permeation chromatographic (GPC) analysis in Examples 1-4 and Comparative Examples 1-5.

Figure 2 shows a relationship of feeding ratio of ϵ -caprolactone/HEMA with a continuous chain distribution ratio of ϵ -caprolactone from a GPC analysis in Examples 5-6 and Comparative Examples 7-11.

BEST MODE FOR CARRYING OUT THE INVENTION

The present inventions I and II are illustrated hereinafter.

The present invention I is comprised a hydroxyalkyl (meth)acrylate composition (a) modified by a small amount of lactones in which a proportion of monomers having two or more pieces ($n \geq 2$) of lactone continuous chains is less than 50% (area % by GPC) which is represented by formula (1), and the composition (a) is a composition obtained by a method for the preparation in the present invention II, that is, a method in which a hydroxyalkyl (meth)acrylate is allowed to react with a lactone in a reaction molar ratio of more than 1 in the case of preparing the polylactone-modified hydroxyalkyl (meth)acrylate

through allowing to react the hydroxyalkyl (meth)acrylate with a lactone monomer by ring-opening polymerization. In more detail, it relates to a composition obtained by allowing to react a lactone with a hydroxyalkyl (meth)acrylate in an atmosphere containing oxygen under the presence of less than 1000 ppm of a catalyst and less than 1% of an inhibitor for preventing polymerization of the hydroxyalkyl (meth)acrylate at a temperature of approximately 80-140°C.

In obtaining the composition (a) of the present invention, a reaction is conducted by feeding lactones at a feeding molar ratio of less than 1 mol with respect to the hydroxyalkyl (meth)acrylate such as hydroxyethylacrylate (HEA) and hydroxyethylmethacrylate (HEMA) in order to decrease lactone continuous chains. The catalyst to be employed in the present invention is a variety of organic and inorganic metal compounds, and preferred catalysts are a tin-based compound such as stannous chloride, monobutyltin tris-2-ethylhexanate, stannous octoate, and dibutyltin dilaurate. By the catalysts, there can be prepared the caprolactone-modified hydroxyalkyl (meth)acrylate composition in which the lactone continuous chains are decreased. In addition to decreasing the lactone continuous chains, although unreacted HEA and HEMA, etc. are remained, since the HEA and HEMA, etc. are often employed alone, if those are not more than 50% by weight, those can be often approved even though a mixed monomer.

Heretofore, in the case that ϵ -caprolactone is ring-opening polymerized on a compound having hydroxyl groups, although the ring-opening polymerization is conducted by adding a titanium-based catalyst such as tetrabutyl titanate, tetraethyl titanate, and tetrapropyl titanate at 130-230°C, even though intending to add ϵ

-caprolactone to a (meth)acrylate having hydroxyl group at temperature conditions of not less than 130°C, the (meth)acrylate itself causes a thermal polymerization, resulting in that it is difficult to obtain a desired product.

In a temperature lower than 130°C, although there can be prevent the thermal polymerization of the (meth)acrylate itself, a ring-opening reaction rate of ϵ -caprolactone becomes very slow.

Since the titanium-based catalyst is relatively strong in catalytic activity, a desired product can be obtained. However, since the catalyst has a strong activity also as a catalyst for transesterification, a transesterification reaction proceeds during the ring-opening polymerization, resulting in that a polyvalent alcohol is removed from 2 mol of the hydroxyalkyl(meth)acrylate, and an alkylene glycol di(meth)acrylate is by-produced.

Since such the di(meth)acrylate has a high boiling point, it is difficult to be separated from a desired product. Moreover, if the desired product containing such a by-product is radically copolymerized in other (meth)acrylates and solvents, three dimensional crosslinking is caused in a resin, and viscosity is remarkably increased or it ends to cause gelation. For that reason, there is desired the use of a catalyst having a strong activity which allows to sufficiently proceed the reaction at a low temperature such as 80-130°C and in a small amount and, moreover, during which the di(meth)acrylate is not produced so much by the transesterification reaction.

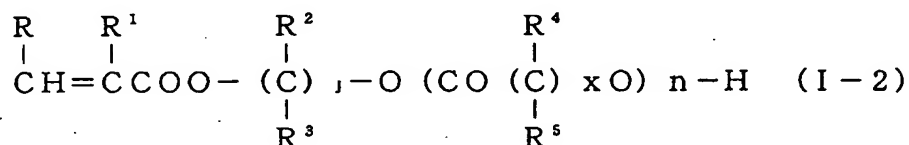
As the catalyst to be employed in the present invention, there can be enumerated a stannous chloride, monobutyltin tris-2-ethyl

hexanate, stannous octoate, and dibutyltin dilaurate, etc. Of those, since there can more decrease discoloration and the transesterification reaction by the use of monobutyltin tris-2-ethylhexanate, concentration of the catalyst can be elevated, and it is also very excellent in view of reduction of reaction time of period.

Addition amount of the catalyst is 1-1000 ppm, and preferably (hereinafter, in this specification, "unpreferably" means "undesirably" or "unfavorably") 10-500 ppm.

As the hydroxyalkyl (meth)acrylate to be employed in the present invention, there are enumerated 2-hydroxyethyl methacrylate, 2-hydroxyethylacrylate, hydroxypropylmethacrylate, hydroxypropylacrylate, 1,4-butyleneglycol monomethacrylate, and 1,4-butyleneglycol monoacrylate, etc.

In the case that 1 mol of a lactone is allowed to react with 1 mol of the hydroxyalkyl (meth)acrylate, a reaction product is obtained as a mixture of compounds represented by a formula described below (I-2) because a ring-opening reaction rate of the lactone to hydroxyl group in the hydroxyalkyl (meth)acrylate nearly equals to a ring-opening reaction rate of the lactone to hydroxyl groups at terminals in a caprolactone which is a product.



(in the formula, R, R¹, R², and R³ are independently a hydrogen atom or a methyl group, "j" is an integer of 2-6, xn pieces of R⁴ and R⁵ are independently a hydrogen atom or an alkyl group having a carbon number of 1-12, "x" is 4-7, "n" is 0 or an integer of not less than

1, and an average value of "n" in the composition is not less than 0.3 to less than 1.0)

In the above-described reaction composition, there statistically distributes an unreacted product having $n=0$ and polycaprolactones having $n=1, 2, 3, 4, 5, \dots$. Herein, it is preferred that n is not more than 2, and an average value of "n" in the reaction composition is not less than 0.3 to less than 1.0, preferably 0.35 to less than 1.0 and, particularly, preferably 0.5 to 0.75.

In the case that the average value of "n" is less than 0.3, adhesion to various materials becomes unpreferably insufficient and, in the case of not less than 1, tackiness becomes too unpreferably strong.

In the case that the mol number of the lactone is not less than 1 mol, there are prepared products having two or more lactone continuous chains and the purpose of the present invention cannot be unpreferably attained. However, since the products cannot be separately refined in an industrial fashion, the amount of lactone to be fed is decreased to less than 1 with respect to 1 mol of the hydroxyalkyl(meth)acrylate in order to decrease the amount of the products having two or more lactone continuous chains. The lactone is allowed to react in not less than 0.3 mol to less than 1.0 mol, preferably not less than 0.35 mol to less than 1.0 mol, and more preferably not less than 0.5 mol to less than 0.75 mol with respect to 1 mol of the hydroxyalkyl(meth)acrylate. In the case of a large amount of the lactone in the reaction, there are produced a large amount of products having long chains of the lactone and, resulting in that the average value of "n" becomes too large and although a reaction curability and flexibility are improved in the use as raw materials for a coating,

there lower hardness and acid resistance in a cured article. Contrarily, it is less than 0.3, the average value of "n" becomes too small and abrasion resistance becomes unpreferably too worse.

Further, as the lactone, there can be employed ϵ -caprolactone, trimethylcaprolactone, δ -valerolactone, γ -butyrolactone, and a mixture thereof.

Reaction temperature is 80-150°C, and preferably 100-140°C.

In the case of lower than 80°C, reaction rate is slow and, in the case of higher than 150°C, there is caused a thermal polymerization of a (meth)acrylate during the reaction, and gelation is possibly caused. In a reaction system, a polymerization inhibitor is preferably added. As the polymerization inhibitor, there are employed hydroquinone, hydroquinone monomethylether, and phenothiazine, etc. in a range of 0.01-1%, and preferably 0.03-0.5%.

In the reaction system, if an inert gas such as nitrogen is streamed, since a radical polymerization is apt to be caused, it is useful that any gases are not streamed or air is streamed in order to prevent the radical polymerization.

In the hydroxyalkyl (meth)acrylate composition modified by a small amount of lactones prepared by a method in the present invention, the content of residual lactones is 0-10% by weight, the content of the residual hydroxyalkyl (meth)acrylate is not less than 20 and not more than 50% by weight at most, the content of the di (meth)acrylate which is a by-product is 2% or less by weight, the content of the by-products by a Michaels addition, a (meth)acrylic polymerization, a transesterification, or other side reactions is not more than 10% by weight, the content of the catalyst is less than 1000 ppm, and the

content of the polymerization inhibitor is not more than 1% by weight.

The lactone-modified acrylate composition having hydroxyl group of the present invention can provide an acrylic polyol of the present invention having rich flexibility which is excellent in reactivity with a crosslinking agent by allowing to polymerize alone or copolymerize with other radically-polymerizable monomers.

Further, the acrylic polyol resin of the present invention is useful as a raw resin for a flexible polyfunctional (meth)acrylate resin coating which includes urethane bonds by allowing to react the acrylic polyol resin of the present invention with polyisocyanates. The acrylic polyol resin of the present invention, as described hereinabove, can be utilized as a raw material for, in addition to the coating, a photo-curable resin, a reactive diluent for the photo-curable resin, a flexibility modifier for an AS and an ABS resin, an acrylic resin, a tackifier, an adhesive, a flexible lens for a glass, an acrylic emulsion (particularly, a reaction type one), a reactive diluent having flexibility instead of styrene in an unsaturated polyester resin, and also materials for a polymerizable polyurethane elastomer, etc.

As the other radically-polymerizable monomers for copolymerizing with the lactone-modified acrylate or methacrylate composition having hydroxyl groups of the present invention, there are enumerated an unsaturated monomer having an isocyanate group, a polymerizable monomer having an active hydrogen, and other polymerizable unsaturated monomers.

The other polymerizable unsaturated monomers are exemplified below.

As (meth)acrylates, for example, there are enumerated an alkyl or cycloalkyl ester having a carbon number of 1-20 of a (meth)acrylic acid such as methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, butyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, octyl(meth)acrylate, lauryl (meth)acrylate, cyclohexyl(meth)acrylate, isobonyl(meth)acrylate, and adamantyl(meth)acrylate; an alkoxyalkyl ester having a carbon number of 2-8 of a (meth)acrylic acid such as methoxybutyl (meth)acrylate, methoxyethyl (meth)acrylate, and ethoxybutyl(meth)acrylate.

As other monomers except the (meth)acrylates, glycidyl(meth)acrylate; styrene, α -methylstyrene, vinyltoluene, (meth)acrylonitrile, (meth)acrolein, butadiene, isoprene, (meth)acrylic acid, etc., and these can be employed in mixing.

As the polymerizable monomer having an active hydrogen, there are enumerated a vinyl monomer having hydroxyl group and a vinyl monomer having amino group, these can be employed in mixing.

As the (meth)acrylate having hydroxyl group, for example, there are enumerated a hydroxyalkyl ester of a (meth)acrylic acid having a carbon number of 2-8 such as 2-hydroxyethyl(meth)acrylate and 2-hydroxypropyl(meth)acrylate, 2-hydroxyethyl vinyl ether, N-methylol(meth)acrylic amide, Alonix 5700 manufactured by Toa Gosei Kagaku Kogyo, Ltd., 4-hydroxystyrene, HE-10, HE-20, HP-10, and HP-20 (all of those are an acrylate oligomer having hydroxyl group at a

terminal) which are manufactured by Nihon Shokubai Kagaku Kogyo, Ltd., Blemmer PP series (a polypropyleneglycol methacrylate), Blemmer PE series (a polyethyleneglycol monomethacrylate), Blemmer PEP series (a polyethyleneglycol-polypropyleneglycol methacrylate), Blemmer AP-400 (a polypropyleneglycol monoacrylate), Blemmer AE-350 (a polyethyleneglycol monoacrylate), Blemmer NKH-5050 (a polypropyleneglycol polytrimethylene monoacrylate), and Blemmer GLM (glycerol monoacrylate) which are manufactured by Nihon Yushi, Ltd., and an ϵ -caprolactone-modified hydroxyalkylvinyl monomer which is obtained by a reaction of a vinyl compound having hydroxyl group with ϵ -caprolactone, etc.

As typical examples of the ϵ -caprolactone-modified hydroxyalkylvinyl monomer, there are enumerated Placel FA-1, Placel FA-4, Placel FM-1, and Placel FM-4, etc. which are manufactured by Daicel Kagaku Kogyo, Ltd., TONE M-100 and TONE M201 which are manufactured by UCC, Ltd., etc., and an average polymerization degree "n" is not less than 1.

As typical examples of the vinyl monomer having amino group, there are enumerated a variety of dialkylaminoalkyl(meth)acrylates such as dimethylaminoethyl(meth)acrylate, diethylaminoethyl(meth)acrylate, diethylaminopropyl(meth)acrylate, and dimethylaminopropyl(meth)acrylate; N-dialkylaminoalkyl(meth)acrylic amides such as N-dimethylaminoethyl(meth)acrylic amide, N-diethylaminoethyl(meth)acrylic amide, N-dimethylaminopropyl(meth)acrylic amide, and N-diethylaminopropyl(meth)acrylic amide; t-butylaminoethyl(meth)acrylate, t-butylaminopropyl(meth)acrylate,

azilidinylethyl(meth)acrylate pyrrolidinylethyl(meth)acrylate, piperidinylethyl(meth)acrylate, vinylpyridine, and aminoethylvinylether, etc. and, the dialkylaminoalkyl(meth)acrylates and N-dialkylaminoalkyl(meth)acrylic amides are particularly preferred from a viewpoint of curability, etc.

As the monomer having isocyanate group, for example, there are enumerated isocyanate ethyl(meth)acrylate, isocyanate propyl(meth)acrylate, isocyanate butyl(meth)acrylate, isocyanate hexyl(meth)acrylate, m-isopropenyl- α , α' -dimethylbenzyl isocyanate, and m-ethylenyl- α , α' -dimethylbenzyl isocyanate, etc., and an unsaturated compound obtained by addition of a polyisocyanate such as hexamethylene diisocyanate compound to the above-described polymerizable monomer having an active hydrogen such as the hydroxyethyl(meth)acrylate, and these can be employed in mixing.

The above-described radically-polymerizable monomers can be also employed in mixing and, those are selectively employed according to desired physical properties.

The acrylic polyol resin of the present invention is prepared by radically-polymerizing the polylactone-modified hydroxyalkylacrylate or methacrylate of the present invention and the above-described radically-polymerizable monomers under the presence of a radical polymerization initiator by publicly-known solution polymerization methods.

As the radical polymerization initiator, there can be employed a peroxide initiator such as benzoyl peroxide, t-butylhydroperoxide, cumylhydroperoxide, cumenhydroperoxide, t-butyl peroxybenzoate, and

t-butylperoxy-2-ethylhexanoate, and an azo-based initiator such as azobisisobutyronitrile and azobisdimethylvaleronitrile.

As solvents for polymerization to be employed in the solution polymerization, if those are a nonreactive solvent, there can be employed hydrocarbons (benzene, toluene, xylene, n-hexane, and cyclohexane, etc.), acetates (ethyl acetate, propyl acetate, and butyl acetate, etc.), alcohols (methanol, ethanol, isopropanol, and n-butanol, etc.), ethers (ethyl cellosolve, butyl cellosolve, and cellosolve acetate, etc.), ketones (methylethylketone, acetoethyl acetate, acetylacetone, diacetone alcohol, methyl isobutyl ketone, and acetone, etc.) without any limitation. The solvents may be employed solely or in combination of two or more kinds.

As a reaction vessel to be employed for the above-described polymerization, there are preferably employed a reaction vessel equipped with an agitation and a reflux condenser equipped with a drying tube and a twin-screw extruder.

Polymerization temperature and polymerization time of period depend upon respective kinds and feeding ratio of the polylactone-modified hydroxyalkyl acrylate or methacrylate composition of the present invention and the above-described radically-polymerizable monomer, kind and amount of the catalyst and, further, reaction vessels, and those are not particularly limited, and those are appropriately decided by the use of a desired acrylic resin, for example, physical properties of a coating layer to be required in the case of a coating.

Hereinafter, the present invention III is illustrated.

The present invention III is a curable resin composition containing an acrylic polyol resin (A) obtained using a hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones in which a proportion of monomers having not less than 2 continuous chains ($n \geq 2$) of lactones is less than 50% (GPC area %), which is represented by the above-described general formula (I) as polymerizing components, and a melamine resin (B).

The hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones is as illustrated in the present invention I.

The acrylic polyol resin (A) to be employed in the present invention is comprised 5-70 parts by weight of the hydroxyalkyl (meth)acrylate composition (a) modified by a small amount of lactones, 0-90 parts by weight of an alkyl(meth)acrylate having an alkyl group of a carbon number of 1-20, 0-30 parts by weight of a (meth)acrylic acid, and 0-40 parts by weight of other polymerizable unsaturated monomer. As the other polymerizable unsaturated monomer, there are enumerated radically-polymerizable monomers other than the alkyl(meth)acrylate as exemplified in the present invention I. Conditions for the preparation thereof are as illustrated in the present invention I.

In the acrylic polyol resin (A), hydroxyl value is 5-250, and a number average molecular weight is 3,000-300,000.

As the melamine resin (B) to be employed in the present invention, there can be employed a usual melamine resin for coating without any modification, and an imino type or methylol type melamine resin is

employed. Since an isocyanate compound is not employed as a curing agent, it is excellent in handling and safeness. The imino type or methylol type melamine resin is not particularly limited, and as a resin capable of reacting with hydroxyl group, if it is a melamine to be employed for a coating system in which hydroxyl group is employed as a functional group, it is not particularly limited. As such the imino type melamine resin, for example, there are enumerated Yuban 22R (solid content of 60%), Yuban 21R (solid content of 50%), and Yuban 2028 (solid content of 75%) (all of those are an imino type melamine resin), etc. which are manufactured by Mitsui Kagaku. On the other hand, as the methylol-type melamine resin, there can be employed a melamine resin having a condensation degree of 1.1-20 or so which is prepared by melamine, formaldehyde, a monoalcohol having a carbon number of 1-4, and optionally, water which are raw materials. For example, there are enumerated Yuban 60R (solid content of 50%) manufactured by Mitsui Kagaku and Superbekkamine L-121-60 (solid content of 60%) manufactured by Dainippon Ink Kagaku Kogyo, Ltd.

The curable resin composition of the present invention contains 0.5-80 parts by weight of the acrylic polyol resin (A) obtained using the composition (a) and 0.5-50 parts by weight of the melamine resin (B). Total of the (A) and the (B) does not exceed 100 parts by weight.

In the case that the acrylic polyol resin (A) is less than 0.5 part by weight, bending resistance becomes insufficient and, in the case of exceeding 80 parts by weight, abrasion resistance unpreferably lowers. In the case that the melamine resin (B) is less than 0.5 part by weight, solvent resistance is not sufficient and, in the case of

exceeding 50 parts by weight, acid resistance becomes unpreferably insufficient.

By another representation of the use ratio of the acrylic polyol resin (A) with respect to the melamine resin (B), 60-10% by weight of the melamine resin (B) is employed together with 40-90% by weight of the acrylic polyol resin (A). In the case that the use ratio of the acrylic polyol resin (A) is less than 40% by weight, a self condensation reaction of the melamine resin (B) itself increases, resulting in that a coating layer becomes brittle and, for example, it does not become appropriate as a coating for a molded article of a polyolefine-based resin. On the other hand, in the case that the use ratio of the acrylic polyol resin (A) exceeds 90% by weight, crosslinking becomes insufficient, and solvent resistance and weatherability lower. A preferred use ratio of the acrylic polyol resin (A) is 60-80% by weight, and the use ratio of the melamine resin (B) is 40-20% by weight.

In the the acrylic polyol resin (A), the melamine resin (B), and the acidic catalyst for curing which is optionally employed in the present invention, total acid value is 5-50, and preferably 15-35. In the case that the total acid value is less than 5, crosslinkable reactivity lowers and crosslinking becomes insufficient, and there lower gasoline resistance and weatherability. On the other hand, in the case that the total acid value exceeds 50, storage stability lowers, and water resistance lowers. As described above, by controlling the acid value, a coating composition can be modified to low temperature curability.

In order to give an acid value to the acrylic polyol resin (A), a monomer having carboxylic group and a phosphoric acid group is employed together as the polymerizable vinyl monomer to introduce the acid groups into the acrylic polyol resin (A). Further, adjustment of the acid value can be conducted by formulating the acidic catalyst for curing into a coating composition. As such the acidic catalyst for curing, a weak acidic catalyst for curing is employed. As such the weak acidic catalyst for curing, for example, there are enumerated phosphoric acids, a monophosphate, a monophosphite, a phosphate containing an unsaturated group, and carboxylic acids, etc. As such the weak acidic catalyst for curing, phosphoric acids and phosphates thereof are particularly preferred. As such the phosphoric acids and phosphates thereof, for example, there are enumerated a phosphoric acid, a pyrophosphoric acid, and a mono or diphosphate, etc. As the monophosphate, for example, there are enumerated monooctyl phosphate, monopropyl phosphate, and monolauryl phosphate, etc. As the diphosphate, for example, there are enumerated dioctyl phosphate, dipropyl phosphate, and diraulyl phosphate, etc. Further, mono(2-(meth)acryloyloxyethyl)acid phosphate is enumerated. Still further, there may be even employed a compound obtained by allowing to react a compound having an acid anhydride group with a polyol or an alcohol. Besides, an oligomer having an acid value may be also blended. In the case, as a method for introducing an acid value into the acrylic polyol resin (A) and other oligomers, for example, there is a method in which there is employed a polymerizable vinyl monomer having carboxylic group or a phosphoric acid group in the case of graft-polymerizing or (co)polymerizing. It is to be noted that the carboxylic group or the phosphoric acid group preferably exists

at not less than 10 atoms-apart position from a main chain of the oligomer, whereby, it readily reacts at a low temperature.

The acidic catalyst for curing is employed in the amount of 0.001-10% by weight, and preferably 0.001-5% by weight based on total weight of the acrylic polyol resin (A) and the melamine resin (B).

The coating composition of the present invention is modified to a coating composition without any modification or by appropriately formulating, optionally, a variety of additives which are conventionally employed in a coating field, for example, coloring pigments, extender pigments, an aluminum powder, a pearl mica powder, an anti-dropping agent or an anti-sedimentation agent, a levelling agent, a dispersant, a defoaming agent, an ultraviolet ray absorbent, a photo-stabilizer, an antistatic agent, and a thinner, etc.

As the coloring pigments, for example, there are enumerated inorganic pigments such as titanium oxide (for example, titanium oxide pigments, Taipek CR-95 (manufactured by Ciba Geigy, AG)), carbon black, iron oxide, iron red, lead molybdenum acid, chromium oxide, and lead chromate, phthalocyanine pigments such as phthalocyanine blue and phthalocyanine green, organic pigments such as quinaklidone red, azo pigments, and anthraquinone pigments, etc.

As the extender pigments, for example, there can be employed kaoline, talc, silica, mica, barium sulphate, and calcium sulphate, etc. As the anti-dropping agent or an anti-sedimentation agent, for example, there can be preferably employed bentonite, a linseed oil wax, an amide wax, micro gel (for example, MG100S (manufactured by Dainippon Ink)), and an aluminum acetate, etc.

As the levelling agent, for example, there can be preferably employed a silicone-based surface active agent such as KF69, Kp321, and Kp301 (hereinafter, manufactured by Shin-etsu Kagaku), Modaflow (a surface controlling agent manufactured by Mitsubishi Monsanto), BYK301, and 358 (manufactured by Bickchemie Japan), and Diaaide AD9001 (manufactured by Mitsubishi Rayon), etc.

As the dispersant, for example, there can be preferably employed Anti-Terra U or Anti-Terra P and Disperbyk-101 (hereinafter, manufactured by Bickchemie Japan), etc.

As the defoaming agent, for example, there can be preferably employed BYK-0 (manufactured by Bickchemie Japan), etc.

As the ultraviolet ray absorbent, for example, there can be preferably employed a benzotriazole-based ultraviolet ray absorbent such as Tinuvin 900, Tinuvin 384, and Tinuvin P (hereinafter, manufactured by Ciba Geigy), an anilide oxalate-based ultraviolet ray absorbent such as Sandbar 3206 (manufactured by Sand), etc.

As the photo-stabilizer, for example, there can be preferably employed a hindered amine-based photo-stabilizer such as Sanol LS292 (manufactured by Sankyo) and Sandbar 3058 (manufactured by Sand), etc.

As the thinner, for example, there can be preferably employed an aromatic compound such as toluene, xylene, and ethylbenzene, alcohols such as methanol, ethanol, propanol, butanol, and isobutanol, ketones such as acetone, methylisobutyl ketone, methylamyl ketone, cyclohexanone, isophorone, and N-methylpyrrolidone, ester compounds such as ethyl acetate, butyl acetate, and methylcellosolve, or a mixture thereof, etc. As the antistatic agent, for example, there can be preferably employed Esocard C25 (manufactured by Lion Armer), etc.

In the case of preparing the coating composition of the present invention, there are mixed the acrylic polyol resin (A), the melamine resin (B), and optionally, additives such as acidic catalysts and pigments, and uniformly dispersed by a dispersing machine such as a sandgrind mill, a ball mill, and an attritor to prepare (a curable coating composition) of the present invention.

As a method for coating the curable coating composition (a coating composition) of the present invention, an article to be coated is coated using a publicly-known dewaxing cleaning apparatus, for example, after dewaxing by an organic solvent such as 1,1,1-trichloroethane, cleaning by an alkali, cleaning by an acid, wiping by a solvent, etc., further, optionally, in order to further elevate an adhesive power of a coating to the article to be coated, for example, the coating composition of the present invention is directly coated by an air-spraying coating method and an airless coating method after coating a primer such as Primac NO. 1500 (manufactured by Nihon Yushi), and optionally, it is set for 0.5-120 minutes, and preferably 1-20 minutes, and thermally cured (baked) at a low temperature of 90-140°C, and preferably 100-120°C.

A clear coating may be coated onto a base coat coating which is an under layer by a wet-on-wet method. In the present invention, since curing can be conducted at a low temperature of not more than 140°C by the above-described construction, it does not give a damage even on a polyolefine-based resin molded article, and there can be formed a coating layer having excellent properties of a coating layer.

In the case that a primer is coated, layer thickness after drying is generally 3-20 μm , and preferably 5-15 μm . Further, layer thickness

after drying of the clear coat coating is generally 15-45 μ m, and preferably 20-35 μ m. As a method for the coating composition of the present invention, there are enumerated a 2-coat/1-baking type coating method and 3-coat/2-baking type coating method, etc.

Herein, the 2-coat/1-baking type is one of coating methods by an over coating and, first of all, there is coated a base coat coating in which pigments and/or metal powder are formulated in a large amount and, there is coated a transparent clear coating or a top coating which is a color clear coating containing a small amount of pigments, and those coatings are simultaneously baked.

In the case of the 2-coat/1-baking type coating method, as a base coat, a usual coating composition is employed and, the coating composition of the present invention can be employed as a top coat.

In the case of the 3-coat/2-baking type coating method, there is coated and baked a coating in which there are formulated pigments, dyes, and metal powder and, there is further coated thereon and baked a base coat in which there are formulated pigments, dyes and/or metal powder, and then, there is coated thereon and collectively baked a transparent clear coating or a top coat which is a color clear coating containing a small amount of pigments or dyes.

IV.

Hereinafter, the present invention IV is illustrated.

The melamine curable type water-based coating composition of the present invention IV is comprised 5-60 parts by weight of an acrylic polyol resin (A) and 10-60 parts by weight of an amino-plasto resin (IV-B), and preferably, 10-50 parts by weight of an acrylic polyol resin (A) and 20-40 parts by weight of an amino-plasto resin (IV-B).

The acrylic polyol resin (A) to be employed in the present invention can provide an acrylic polyol resin (A) which is excellent in reactivity with a crosslinking agent and rich in flexibility by allowing to polymerize alone the hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones represented by the above-described general formula (1) or to copolymerize with other radically-polymerizable monomers, and it can be employed as a material for the melamine curable type water-based coating composition of the present invention.

As other radically-polymerizable monomers for copolymerizing with the hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones in the present invention, there can be employed at least one or more kinds selected from the group consisting of (b) - (i) described below.

- (b) a polymerizable monomer containing an active hydrogen.
- (c) an N-alkoxymethyl(meth)acrylic amide having an alkyl group of a carbon number of 1-6.
- (d) an alkyl(meth)acrylate having an alkyl group of a carbon number of 1-20.
- (e) an aliphatic or cycloaliphatic vinyl monomer having a carbon number of 2-12.
- (f) an aromatic vinyl monomer.
- (g) an adduct of a glycidyl ester of a (meth)acrylic acid with a fatty acid having a carbon number of 8-20.
- (h) an adduct of a (meth)acrylic acid with an monoepoxy compound having a carbon number of 8-20.
- (i) an unsaturated monomer containing an isocyanate group.

As the polymerizable monomer containing an active hydrogen (b), there are enumerated a (meth)acrylate having hydroxyl group, a (meth)acrylate having amino group, and α, β -ethylenic unsaturated carboxylic acid (b), etc., which are described hereinafter.

As the (meth)acrylate having hydroxyl group, for example, there are enumerated hydroxyalkyl (meth)acrylates having a carbon number of 2-8 such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, and 4-hydroxybutyl (meth)acrylate, and those can be employed in mixing.

As the (meth)acrylate having amino group, for example, there are enumerated amino alkyl esters such as dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, (meth)acrylic amide, and N-isopropylmethyl (meth)acrylic amide, etc.

Further, N,N-dimethylaminoethyl (meth)acrylate and dimethyl (meth)acrylic amide, etc. are employed together.

As the α, β -ethylenic unsaturated carboxylic acid, there are enumerated ethylenic unsaturated carboxylic acids such as acrylic acid, methacrylic acid, crotonic acid, maleic acid (anhydride), itaconic acid (anhydride), and fumaric acid.

As the N-alkoxymethyl (meth)acrylic amide (c) having an alkyl group of a carbon number of 1-6, there are enumerated N-methoxy (meth)acrylic amide, N-ethoxymethyl (meth)acrylic amide, N-butoxymethyl (meth)acrylic amide, etc., and N-methoxymethyl acrylic amide is preferred. Further, use amount thereof is 1-25% by weight in a water-based acrylic resin. In the case of less than 1% by weight, water resistance of a coating layer becomes insufficient because of lack of curability and, in the case of not less than 25% by weight,

adhesion and processability are poor, and an aesthetic market value lowered because of a remarkable discoloration in a coating layer.

As the alkyl(meth)acrylate (d) having an alkyl group of a carbon number of 1-20, for example, there are enumerated an alkyl or cycloalkyl(meth)acrylate having a carbon number of 1-20, such as methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, butyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, octyl(meth)acrylate, lauryl(meth)acrylate, cyclohexyl(meth)acrylate, isobonyl(meth)acrylate, and adamantyl(meth)acrylate. As alkoxyalkylester (d') having an alkyl group of a carbon number of 2-8, there are enumerated methoxybutyl(meth)acrylate, methoxyethyl(meth)acrylate, and ethoxybutyl(meth)acrylate.

As the aliphatic or cycloaliphatic vinyl monomer (e) having a carbon number of 2-12, there are enumerated (meth)acrylonitrile and (meth)acrolein; butadiene and isoprene; vinyl esters or isopropenyl esters such as vinylacetate, vinylpropionate and isopropenyl acetate; vinylethers such as ethyl vinylether, butyl vinylether, cyclohexyl vinylether, and phenylvinyl ether.

As the aromatic vinyl monomer (f), there are enumerated styrene, α -methylstyrene, and vinyl toluene, etc.

As the glycidyl ester (g) of a (meth)acrylic acid, for example, there is enumerated a glycidyl(meth)acrylate, etc.

As the adduct (g') of a glycidyl ester of a (meth)acrylic acid with a fatty acid having a carbon number of 8-20, there is enumerated an adduct of a glycidyl(meth)acrylate with a fatty acid having a carbon number of 8-20 such as oleic acid, lauric acid, and stearic acid.

As the adduct (h) of a (meth)acrylic acid with a monoepoxy compound having a carbon number of 8-20, there is enumerated an adduct of a (meth)acrylic acid with Kardula E10 (a glycidyl ester of a branched higher fatty acid manufactured by Shell Chemicals, Ltd.).

As the monomer (i) containing an isocyanate group, for example, there are enumerated isocyanate ethyl(meth)acrylate, isocyanate propyl(meth)acrylate, isocyanate butyl(meth)acrylate, isocyanate hexyl(meth)acrylate, m-isopropenyl- α, α' -dimethylbenzyl isocyanate, and m-ethylenyl- α, α' -dimethylbenzyl isocyanate, etc., and further, an unsaturated compound in which a polyisocyanate compound such as hexamethylene diisocyanate is added to the above-described polymerizable monomer containing an active hydrogen such as hydroxyethyl(meth)acrylate and, those can be employed in mixing.

The above components (b)-(i) can be employed by mixing of one or more kind in or between respective components.

In the acrylic polyol resin (A), for example, there can be preferably employed 3-40% by weight of the hydroxyalkyl (meth)acrylate composition (a) modified by a small amount of lactones, 1-20% by weight of the α, β -unsaturated carboxylic acid, 1-25% by weight of the N-alkoxymethyl(meth)acrylate having an alkyl group of a carbon number of 1-6, and the aromatic vinyl monomer and the alkyl(meth)acrylate in the residual amount which is that 100% by weight minus total amount of the above.

In the acrylic polyol resin (A), for example, preferably, a number average molecular weight is 2,000-50,000, a hydroxyl value is 10-150 mg-KOH/g, and Tg point is 0-60°C.

The acrylic polyol resin (A) to be employed in the present invention is as illustrated in the present invention I.

Amino-plasto resin (IV-B)

Melamine resin (j) is at least one kind of a guanamine resin (k) selected from the group consisting of benzoguanamine, spiroguanamine, acetoguanamine, and phthaloguanamine; and/or a melamine-guanamine cocondensation resin (I), and it is partially etherized by a monovalent alcohol having a functional group of a carbon number of 1-6.

As the alcohol, for example, there is employed an alkyl alcohol having a carbon number of 1-4 such as methanol, ethanol, n-propanol, isopropanol, n-butanol, and isobutanol, etc., alone or in mixing.

Specifically, there are enumerated a methyletherized methylol melamine resin, a methyletherized methylol benzoguanamine resin, a methyletherized melamine-benzoguanamine cocondensation resin, a butyletherized methylol melamine resin, a butyletherized methylol benzoguanamine resin, and a methoxy-ethoxy mixed etherized benzoguanamine resin, etc. Of those, there are particularly preferred the methyletherized, and methoxy-ethoxy mixed etherized or methoxy-ethoxy mixed etherized melamine-benzoguanamine copolymerized resin from a viewpoint of retort resistance and processability.

The melamine curable type water-based coating composition of the present invention is comprised 5-60 parts by weight of an acrylic polyol resin (A) and 10-60 parts by weight of an amino-plasto resin (IV-B), and preferably, 10-50 parts by weight of an acrylic polyol resin (A) and 20-40 parts by weight of an amino-plasto resin (IV-B). In the case that the acrylic polyol resin (A) is less than 5 parts by weight, hardness

of a coating layer remarkably lowers and, in the case of exceeding 60 parts by weight, retort resistance is unpreferably deteriorated. In the case that the amino-plasto resin (IV-B) is less than 10 parts by weight, curability lowers and, in the case of exceeding 60 parts by weight, processability unpreferably lowers.

The alkyletherized melamine resins are employed in an amount of 5-40% by weight in an over coat coating. In the case that the amount of the alkyletherized melamine resins is less than 5% by weight, a crosslinking reaction does not sufficiently proceed, and there lower solvent resistance and acid rain resistance. Further, in the case of exceeding 40% by weight, flexibility lowers in a coating layer, and there lowers bending resistance and impact resistance. In the case that the alkyletherized melamine resins alone are employed as a crosslinking agent, the alkyletherized melamine resins are employed in an amount of 20-40% by weight in an over coat coating. In the case of being less than 20% by weight, a crosslinking reaction does not sufficiently proceed, and there lower solvent resistance and acid rain resistance.

It is to be noted that it is preferred to optionally employ together a blocked polyisocyanate compound as a crosslinking agent.

By the use thereof, use amount of the alkyletherized melamine resins can be reduced and, a staining resistance is further improved owing to a relative decrease of an ether bond. Use amount thereof is 20% by weight at most, and in the case that it is formulated in exceeding 20% by weight, there lowers curability at a low temperature unpreferably.

As the blocked polyisocyanate compound, there are exemplified

a polyhexamethylene diisocyanate which is an active methylene compound isocyanurate type and a polytetramethyl xylilene diisocyanate which is a methylethylketoxime blocked adduct type.

In the melamine-curable water-based coating composition of the present invention, there can be optionally employed an acidic catalyst, or amine-block agent thereof, for example, p-toluene sulphonic acid, dodecylbenzene sulphonic acid, dinonylnaphthalene sulphonic acid, and an amine blocking agent thereof in an amount of 0.1-4.0 parts by weight based on 100 parts by weight of solid content of resins as a curing catalyst. Likewise, there can be also added a defoaming agent, a leveling agent, and a lubricant, etc.

Further, there can be added pigments such as titanium oxide, an aluminum pigment, and quinaklidone by dispersing and kneading in the above-described water-based acrylic resin or a mixture of the water-based acrylic resin with other water-based resin using a publicly-known dispersing machine such as a sandmill or disper to prepare a pigment paste, followed by preparing a coating using the same method described hereinabove.

Still further, the melamine curable type water-based coating composition can be mixed with a water-soluble resin and a water-dispersible resin, for example, a resin such as a polyester, a polyetherpolyol, a polyesterpolyol, a polyurethanepolyol, a maleic-modified fatty acid, and an adduct of ethyleneoxide or propyleneoxide to bisphenol A, which are usually employed.

Furthermore, in the melamine curable type water-based coating composition, there can be also mixed an acrylic resin having a glass transition temperature of exceeding 0°C or an acrylic resin having a

glass transition temperature of not more than 0°C according to uses thereof.

The melamine curable type water-based coating composition can be coated on a substrate by publicly-known means such as a roll coating, spray coating, and brush coating, etc.

A metallic base plate includes an extended steel plate, a stainless steel plate, and an aluminum alloy plate which have a plate thickness of 0.01-2.0 mm. In the metallic plates, surface is treated by at least one or more kinds of alloy or a composite which include an inorganic metal such as chromium, tin, zinc, and nickel an organic material such as an acrylic resin, using such as methods as plating, vapor deposition, coating, zirconium, alumite, and phosphate, etc. Further, there can be employed a metal plate in which a resin film such as a polyethylene terephthalate or a polybutylene terephthalate is laminated with the plates.

Hereinafter, the present invention IV is illustrated.

The present invention IV is a curable resin composition containing an acrylic polyol resin (V-A) obtained using a hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones in which a proportion of monomers having not less than 2 continuous chains ($n \geq 2$) of lactones is less than 50% (GPC area %), and which is represented by the above-described general formula (1), and a polyisocyanate compound (V-B).

The hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones to be employed in the present invention is

as illustrated in the present invention I.

By allowing to polymerize the hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones to be employed in the present invention alone or copolymerize with other radically-polymerizable monomers, there can be provided an acrylic polyol resin having an excellent reactivity with a crosslinking agent and rich flexibility, and it can be utilized as a material for the curable resin composition for a coating of the present invention.

As the other radically-polymerizable monomers to be copolymerized with the (meth)acrylate composition having hydroxyl group modified by a small amount of lactones to be employed in the present invention, there are enumerated a polymerizable monomer having an active hydrogen and other polymerizable unsaturated monomers, which include monomers exemplified in the present invention I.

The other radically-polymerizable monomers can be also employed in mixing, and those are selectively employed depending upon desired physical properties.

Preferably, the acrylic polyol resin (V-A) is comprised 5-65% by weight of the hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones, 0-30% by weight of the vinyl monomer having hydroxyl group, and other vinyl-based monomers of a residual amount which is that 100% by weight minus total amount of the above monomers.

The acrylic polyol resin (V-A) to be employed in the present invention is prepared according to the methods in the present invention II.

The polyisocyanate compound (V-B) to be employed in the present invention is an aromatic, aliphatic, and cycloaliphatic polyisocyanate and, there are preferred an aromatic polyisocyanate having a carbon number of 6-30, an aliphatic polyisocyanate having a carbon number of 4-30, and a cycloaliphatic polyisocyanate having a carbon number of 8-30. For example, there are typically enumerated 2,4-naphthalene diisocyanate, 1,5-naphthalene diisocyanate, 4,4'-diphenylmethane diisocyanate, 4,4'-diphenyldimethylmethane diisocyanate, dialkyldiphenylmethane diisocyanate, tetraalkyldiphenylmethane diisocyanate, 4,4'-diphenylenemethane diisocyanate, 4,4'-dibenzyl diisocyanate, 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, a tolylene diisocyanate such as 2,4-tolylene diisocyanate and 2,6-tolylene diisocyanate, xylilene diisocyanate such as p-xylilene diisocyanate and m-xylilene diisocyanate, 1,4-tetramethylene diisocyanate, 1,5-pentamethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethylhexamethylene-1,6-diisocyanate, 2,4,4-trimethylhexamethylene-1,6-diisocyanate, ridine diisocyanate, cyclohexane-1,4-diisocyanate, isophorone diisocyanate, 4,4'-diisocyanatedicyclohexane, 4,4'-diisocyanate dicyclohexane, dicyclohexylmethane-4,4'-diisocyanate, 1,3-bis(isocyanatemethyl)cyclohexane, and methyl cyclohexane diisocyanate such as methyl cyclohexane-2,4- (or -2,6-) diisocyanate, etc., or an adduct of the diisocyanates to a polyvalent alcohol such as ethylene glycol, propylene glycol, a polyethylene glycol, a polypropylene glycol, a polycaprolactone polyol, trimethylol ethane, and trimethylol propane, a polyester resin (including an oil-modified type) having a functional group which reacts with isocyanate group,

an acrylic resin, etc., and water, etc., a buret compound, a polymer allowed to react between isocyanates, or an equal mol adduct of 2-hydroxypropyl (meth)acrylate-hexamethylene diisocyanate, a copolymer essentially containing a vinyl-based monomer having a copolymerizable unsaturated group with an isocyanate group such as isocyanateethyl (meth)acrylate, or compounds described in JP-A-61072013 Official Gazette, and a blocked compound blocked by a blocking agent such as a lower monovalent alcohol, phenols, methylethylketoxime, and a lactam, etc.

The diisocyanates may be employed solely or even in combination of two or more kinds.

From a viewpoint of a color tone in a coating layer obtained using the curable resin composition of the present invention, as a polyisocyanate compound, nonyellowing type polyisocyanates are preferred, and the following ones are disclosed as an example.

There are enumerated aliphatic-based polyisocyanates such as 1,4-tetramethylene diisocyanate, 1,5-pentamethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylenediisocyanate, and ridine diisocyanate; cycloaliphatic-based polyisocyanates such as isophorone diisocyanate, methyl cyclohexane-2,4-(or -2,6-)diisocyanate, dicyclohexyl methane-4,4'-diisocyanate, and 1,3-bis(isocyanatemethyl) cyclohexane, and the above-described derivatives (including an adduct) therefrom. Of those, there are preferably enumerated 1,6-hexamethylene diisocyanate (hereinafter, abbreviated as HMDI), isophorone diisocyanate (hereinafter, abbreviated as IPDI), and a derivative (including an adduct) therefrom

in view of weatherability and an ease of industrially-obtaining.

Since the polyisocyanate compounds react with polyols in a base material even at room temperatures, those include a drawback that those are poor in storage stability, and handling is troublesome and, those are unpreferred in view of safeness and hygiene. Accordingly, blocked type polyisocyanates are preferred as the polyisocyanate compounds.

Although the blocked type polyisocyanates (hereinafter, occasionally referred to as a highly-branched block polyisocyanate) are obtained even only by allowing to react the polyisocyanates with a polyvalent alcohol, more preferably, those can be obtained by cyclic trimerization of an isocyanate, that is, isocyanuration after allowing to react a diisocyanates with the polyvalent alcohol.

As the polyvalent alcohol in the case, there is preferred an alcohol having three or more functionalities and, as a polyvalent alcohol having a low molecular weight, for example, there are enumerated trimethylol propane, glycerine, 1,1,7-trimethylol heptane, 1,2,7-trimethylol heptane, and pentaerythritol, etc. As a polyvalent alcohol having a higher molecular weight, for example, there are enumerated aliphatic hydrocarbon polyols, polyether polyols, polyester polyols, and epoxy resins, etc.

As the aliphatic hydrocarbon polyols, for example, there are enumerated a polybutadiene having hydroxyl group at terminals and a hydrogenate product therefrom, etc. Further, as the polyether polyols, for example, there are enumerated so-called polymer polyols, etc. obtained by polymerizing acrylic amides in media which are polyether polyols in which an alkylene oxide such as ethyleneoxide or propyleneoxide is added alone or in a mixture to polyvalent alcohols

such as glycerine or propyleneglycol, polytetramethylene glycols, or polyethers in which polyfunctional compounds such as ethylenediamine or ethanolamines are added to an alkylene oxide.

As the polyester polyols, there are enumerated polyester polyol resins obtained by condensation reaction of at least one of a polybasic acid with at least one of polyvalent alcohols, and polycaprolactones obtained by ring-opening polymerization of ϵ -caprolactone using polyvalent alcohols.

As the polybasic acid, for example, there are enumerated phthalic acid (anhydride), terephthalic acid, isophthalic acid, tetrahydrophthalic acid (anhydride), hexahydrophthalic acid (anhydride), 3-methylhexahydrophthalic acid (anhydride), 4-methylhexahydrophthalic acid (anhydride), 3-methyltetrahydrophthalic acid (anhydride), trimellitic acid (anhydride), pyromellitic acid (anhydride), het acid (anhydride), hymic acid (anhydride), adipic acid, sebacic acid, azelaic acid, succinic acid (anhydride), maleic anhydride, fumaric acid, itaconic acid, and a dimer acid, etc. The acid may be employed even in the form of an ester of a lower alcohol such as dimethylisophthalate and dimethylterephthalate.

The polyvalent alcohols are a compound having at least two alcoholic or phenolic hydroxyl groups in the molecule, for example, there are specifically enumerated ethylene glycol, diethylene glycol, triethyleneglycol, polyethyleneglycol, 1,6-hexanediol, pentanediol, cyclohexane dimethanol, propylene glycol, butylene glycol, butylene diglycol, trimethylol ethane, trimethylol propane, glycerine, neopentyl glycol, sorbitol, tris(2-hydroxyethyl)isocyanurate,

diethanol amine, diisopropanol amine, bisphenol A, and bisphenol F, etc.

As the epoxy resins, for example, there are enumerated a novolak type, β -methylepichlorohydrin type, a cyclic oxirane type, a glycidylether type, a glycolether type, an epoxy type of an aliphatic unsaturated compound, an epoxidized fatty acid ester type, a polycarboxylic acid ester type, an aminoglycidyl type, a halogenated type, and resorcinol type, etc.

Of the polyols, there are preferably employed the above-described polyvalent alcohol having a low molecular weight and a polyether polyol having 3-8 pieces of hydroxyl groups in the molecule, the aliphatic hydrocarbon polyols, and polyester polyols and, particularly preferably, the polyester polyols. These may be employed solely or in combination of two or more kinds. Aliphatic or cycloaliphatic diisocyanate and the polyvalent alcohols are allowed to react at 50-200°C, and preferably 50-150°C. In the case, solvents may be even employed, and there are preferably employed solvents which are inactive to an isocyanate. As such the inactive organic solvents, for example, there are employed at least one kind of aliphatic hydrocarbons such as hexane, heptane, and octane; aromatic hydrocarbons such as benzene, toluene, and xylene; esters; and ketones. Since the solvents occasionally contain moisture, it is preferred to optionally remove the moisture. Although the reaction can be conducted even after an isocyanuration reaction, it is preferably conducted prior to the isocyanuration reaction.

In the isocyanuration reaction, catalysts are usually employed. In usual, the catalysts to be employed herein are preferably basic,

for example, there are employed a quaternary ammonium salts and a weak organic acid salt thereof, an alkyl metal salt of an alkyl carboxylic acid, an metal alcoholate, and a compound having an aminosilyl group, etc. Concentration of the catalysts is usually selected from a range of 210 ppm to 1.0% based on isocyanate compounds.

In the reaction, solvents may be employed or even not employed. In the case that the solvents are employed, there should be employed solvents which are inert to an isocyanate group.

Reaction temperature is usually 20-160°C, and preferably 40-130°C. Termination point of the reaction depends upon the kind of the polyvalent alcohols to be employed, and it is a period at which yield attains to approximately 30%. When the reaction attains to a target yield, for example, the reaction is terminated by deactivation of the catalysts by, for example, sulphonic acid, phosphoric acid, and phosphates, etc.

In a highly-branched polyisocyanate having an isocyanurate structure after removal of unreacted diisocyanates and solvents, viscosity at 25°C is preferably 0.5 to 300 Pas. In the case that the viscosity exceeds 300 Pas, outer appearance in a coating layer is adversely affected occasionally and, in the case of being less than 0.5 Pas, it is difficult to obtain a range of an average functional group number of the polyisocyanate regulated in the present invention.

As a blocking agent for obtaining the highly-branched block polyisocyanate, for example, there are enumerated phenol-based ones such as phenol, cresol, xylenol, ethylphenol, o-isopropylphenol, butylphenol such as p-tert-butylphenol, p-tert-octylphenol, nonylphenol, dinonylphenol, styrenized phenol, oxybenzoic acid phenol,

thymol, p-naphthol, p-nitrophenol, p-chlorophenol; alcohol-based ones such as methanol, ethanol, propanol, butanol, ethyleneglycol, methylcellosolve, butylcellosolve, methylcarbitol, benzyl alcohol, phenylcellosolve, fulfurylalcohol, and cyclohexanol; active methylene-based ones such as dimethyl malate, diethyl malate, methylacetoacetate, ethylacetoacetate, and acetyl acetone; mercaptan-based ones such as butyl mercaptan, thiophenol, and tert-dodecyl mercaptan; amine-based ones such as diphenyl amine, phenylnaphtyl amine, aniline, and carbazole; acid amide-based ones such as acetanilide, acetoanisidide, amide acetate, and benzamide; lactam-based ones such as ϵ -caprolactam, δ -valerolactam, γ -butyrolactam, and β -propiolactam; acid imide-based ones such as succinic acid imide and maleic acid imide; imidazole based ones such as imidazole, 2-methylimidazole, and 2-ethylimidazole; urea-based ones such as urea, thiourea, an ethylene urea; carbamide acid salt-based ones such as N-phenylcarbamic acid phenyl and oxazolidone; imine-based ones such as ethyleneimine and a polyethylene imine; oxime-based ones such as formaldoxime, acetoaldoxime, acetoxime, methylethylketoxime, methylisobutylketoxime, and cyclohexanoeoxime; bisulphite-based ones such as sodium bisulphite and potassium bisulphite, etc., and these may be even as a mixture.

Of those, there are preferred the phenol-based ones, lactam-based ones, alcohol-based ones, and oxime-based ones and, there are particularly preferred nonylphenol, styrenized phenol, oxybenzoic acid ester, acetoxime, methylethylketoxime, and ϵ -caprolactam.

In the case that a low temperature (not more than 140°C) baking is demanded, particularly, an oxime-based blocking agent is most

preferred.

By allowing to react the blocking agent with the highly-branched polyisocyanate, the highly-branched block polyisocyanate can be obtained. Reaction of the isocyanate with the blocking agent can be conducted regardless of the presence or absence of solvents.

In the case that the solvents are employed, there must be employed solvents which are inert to an isocyanate group.

In the reaction for blocking, there may be even employed catalysts such as organic salts of metals such as tin, zinc, lead, and a tertiary amine, etc. The reaction can be conducted at -20 to 150°C and, preferably, 0 to 100°C. In the case of exceeding 100°C, side reactions are possibly caused and, on the other hand, in the case of too low temperatures, reaction rate becomes slow, and it is disadvantageous.

The block polyisocyanate to be employed in the present invention has the average number of functional group of 4.5-10, preferably, 5-8 per 1 molecule of the block polyisocyanate.

The average number of functional group in the block polyisocyanate is a number of an isocyanate functional group to be statistically possessed in 1 molecule of the block polyisocyanate, and it is calculated by the following equation (1) from a number average molecular weight of the polyisocyanate before the blocking reaction and an isocyanate concentration (%).

$$(\text{Number average molecular weight}) \times \frac{(\text{isocyanate concentration})}{100}$$

molecular weight of isocyanate group (42)

= Average number of an isocyanate functional group Equation (1)

The acrylic polyol resin (V-A) and the polyisocyanate compound (V-B) in the present invention are employed as a raw material for a coating, which construct a primary component in the curable resin composition of the present invention. Equivalent ratio of the isocyanate group in the polyisocyanate or the blocked isocyanate group with respect to hydroxyl group in the resin containing hydroxyl groups is decided according to physical properties of a coating layer to be desired.

Formulation ratio of the acrylic polyol resin (V-A) with respect to the polyisocyanate compound (V-B) in the present invention is preferably $\text{NCO/OH}=0.8-1.3$ (equivalent ratio) from a viewpoint of properties in a coating layer. In the case that the NCO/OH is less than 0.8, residual hydroxyl group occasionally causes a decline of water resistance in a coating layer and, in the case of exceeding 1.3, residual isocyanate group unpreferably makes the coating layer brittle.

The curable resin composition of the present invention contains 50-90 parts by weight of the acrylic polyol resin (V-A) and 10-50 parts by weight of the polyisocyanate compound (V-B) as essential components, provided that total of the (V-A) and the (V-B) does not exceed 100 parts by weight.

Use ratio of the acrylic polyol resin (V-A) with respect to the polyisocyanate compound (V-B) is 50-10 parts by weight of the polyisocyanate compound (V-B) with respect to 50-90 parts by weight of the acrylic polyol resin (V-A). In the case that the use ratio of the acrylic polyol resin (V-A) is less than 50 parts by weight, a coating layer becomes brittle, for example, resulting in that it becomes not appropriate as a coating for a molded article of a polyolefine-based

resin.

On the other hand, in the case that the use ratio of the acrylic polyol resin (V-A) exceeds 90 parts by weight, crosslinking becomes insufficient and, resulting in that there lower water resistance, solvent resistance, and weatherability. A preferred use ratio of the acrylic polyol resin (V-A) is 60-80 parts by weight, accordingly, a preferred use ratio of the polyisocyanate compound (V-B) becomes 40-20 parts by weight

In the present invention, an acidic catalyst for curing is employed in order to cure by allowing to react the acrylic polyol resin (V-A) with the polyisocyanate compound (V-B).

Total acid value of in the acidic catalyst for curing is 5-50, and preferably 15-35. In the case that the total acid value is less than 5, crosslinking reactivity lowers, resulting in that crosslinking becomes insufficient, and there lower gasoline resistance and weatherability.

On the other hand, the acid value is higher than 50, there lower storage stability and water resistance.

As described hereinabove, a coating composition can be changed to a lower temperature curability by controlling the acid value. As such the acidic catalyst for curing, a weak acidic catalyst is employed. As such the weak acidic catalyst, for example, there are enumerated phosphoric acids, a monophosphate, a phosphite, a phosphate having an unsaturated group, and carboxylic acids, etc.

As the weak acidic catalyst, the phosphoric acids and phosphates are particularly preferred. As such the phosphoric acids and phosphates,

for example, there are enumerated phosphoric acid, pyrophosphoric acid, etc., and mono or diphosphates, etc. As the monophosphates, for example, there are enumerated monooctyl phosphate, monopropyl phosphate, and monolauryl phosphate, etc. As the diphosphates, for example, there are enumerated dioctyl phosphate, dipropyl phosphate, and dilauryl phosphate, etc.

The acidic catalyst for curing is employed in an amount of 0.001-10% by weight, and preferably 0.001-5% by weight based on total weight of the acrylic polyol resin (V-A) and the polyisocyanate compound (V-B).

In the case that the polyisocyanate is prepared as a block type, it is a single-liquid type and, although there can be solved a problem concerning storage stability, dissociation temperature of the blocking agent becomes high and, it must become occasionally heated to not less than 150°C, and there is occasionally caused a problem that compatibility with a base resin is not sufficient and, an outer appearance in finishing becomes worse in a coating layer.

In the cases, the polyisocyanate compound to be employed in the present invention is preferably employed as a self-crosslinkable type resin which simultaneously contains a block isocyanate group and hydroxyl group in a molecule, which is described hereinafter.

The self-crosslinkable type resin is comprised a product in which a vinyl polymer having a block isocyanate group in a molecule is connected to a polyol resin having hydroxyl group in the molecule through urethane bond and, for example, it is obtained by (I) allowing to react a portion of hydroxyl groups in the polyol resin (A0) having at least two hydroxyl

groups in the molecule with a portion of free isocyanate groups in a vinyl polymer (B0) having at least two free isocyanate groups in the molecule, and then, allowing to react a blocking agent with residual all the free isocyanate groups, or (II) allowing to react a portion of hydroxyl groups in the polyol resin (A0) having at least two hydroxyl groups in the molecule with all of free isocyanate groups in a vinyl polymer simultaneously having free isocyanate groups and block isocyanate groups in the molecule.

The vinyl polymer (B0) is a vinyl polymer having at least two free isocyanate groups in the molecule and, specifically, it is a polymer in which a vinyl monomer containing isocyanate group (hereinafter, abbreviated as "NCO group-contained monomer") is employed as an essential component, and further, other monomers are optionally employed, and which has isocyanate groups at terminals and/or side chains in a linear chain polymer.

The NCO group-contained monomer is a compound having at least one of a nonblocked free isocyanate group and at least one of a radically-polymerizable double bond, respectively.

For example, there are employed at least one or two kinds selected from isocyanate methyl methacrylate, 2-isocyanate ethylmethacrylate, m- or p- isopropenyl- α , α' -dimethylbenzyl isocyanate, and a 1:1 (molar ratio) adduct of a vinyl monomer having hydroxyl group with a diisocyanate compound, etc.

The diisocyanate compound has two isocyanate groups in the molecule, and there are enumerated the above-described aliphatic, aromatic, or cycloaliphatic-based diisocyanate compounds.

Of the above compounds, a preferred compound as the NCO group-contained monomer is 2-isocyanate ethylmethacrylate, m-isopropenyl- α, α' -dimethylbenzyl isocyanate, and an equimolar adduct of 2-hydroxyethylacrylate with isophorone diisocyanate, etc.

The vinyl monomer having hydroxyl group, which is employed for preparing the NCO group-contained monomer, is a compound having at least one hydroxyl group and at least one radically-polymerizable double bond, respectively, in the molecule, for example, there are enumerated 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, hydroxybutylacrylate, 2,3-dihydroxypropylacrylate, 2-hydroxy-3-phenoxyethylacrylate, and 2-hydroxy-3-ethoxyethylacrylate, etc. Further, there is enumerated an equimolar adduct of acrylic acid or methacrylic acid with a glycol (a carbon number of 2-20), etc.

The vinyl polymer (B0) is obtained by polymerizing the NCO group-contained monomer alone or by copolymerizing the monomer with other vinyl monomers.

As the other vinyl monomers, there is preferred a compound which contains one radically-polymerizable double bond in the molecule and, moreover, which does not contain an active hydrogen which can react with isocyanate group, specifically, there are enumerated aromatic vinyl-based monomers such as styrene, α -methylstyrene, and vinyltoluene; (meth)acrylates such as methyl(meth)acrylate, ethyl(meth)acrylate, butyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, lauryl(meth)acrylate, tridecyl(meth)acrylate, stearyl(meth)acrylate, cyclohexyl(meth)acrylate,

and benzyl(meth)acrylate; a fluorine-contained vinyl-based monomer such as Viscose 3F (a trade name, manufactured by Osaka Yuki Kagaku, Ltd., hereinafter, it shows a same mean), Viscose 3MF, Viscose 8F, Viscose 8MF, perfluorocyclohexyl(meth)acrylate, N-2-propylperfluorooctane sulphonic amide ethyl(meth)acrylate, vinylfluoride, and vinylidene fluoride; a nitrogen-contained vinyl monomer such as N,N'-diethylaminoethyl(meth)acrylate, N,N'-diethylaminoethyl(meth)acrylate, N,N'-diethylaminoethyl(meth)acrylate, and N,N'-diethyl(meth)acrylic amide; a vinylether-based monomer such as vinylethylether and vinylbutylether; and glycidyl(meth)acrylate, 3,4-epoxycyclohexylmethyl(meth)acrylate, an alkyletherized compound such as arylglycidyl ether and methylol acrylic amide, (meth)acrylic amide, (meth)acrylic chloride, vinylchloride, vinylidenechloride, (meth)acrylonitrile, and γ -methacryloxyalkyl trimethoxy silane, etc., and these are employed solely or as a mixture of two or more kinds.

Ratio of the NCO group-contained monomer with respect to the other vinyl monomers, if it is within a range containing at least two free isocyanate groups in one molecule of the polymer (B0), is not particularly limited, and the NCO group-contained monomer/the other vinyl monomers (weight ratio) ranges in 100/0-1/99, preferably 65/35-30/70.

Further, in usual, a polymerization reaction of the NCO group-contained monomer alone or a copolymerization reaction of the other vinyl monomers is preferably conducted in an inert organic solvent

not having an active hydrogen which can react with isocyanate group. As such the inert organic solvent, there are employed the above-described solvent or a mixture thereof. Since the solvents occasionally contain moisture, the moisture is optionally in advance removed.

The (co)polymerization reaction is usually conducted at a temperature of 50-180°C using a radical polymerization initiator, a molecular weight of the polymer (B0) can be controlled by a reaction concentration and the amount of the radical polymerization initiator, etc. The reaction concentration ranges in 20-80% by weight as a polymer. Particularly, in order to elevate a polymerization ratio, there is employed a peroxide-based or carbonate-based polymerization initiator, and the reaction is preferably conducted at a temperature of not less than 100°C.

More preferably, there is apt to be obtained a polymer having a high polymerization ratio by employing together an acrylate-based monomer. Concentration of the polymerization initiator ranges in 0.01-15% by weight based on total monomers, and it preferably ranges in 0.1-10% by weight.

Further, it can be also polymerized by utilizing an electron beam or ultraviolet ray in place of employing the polymerization initiator.

Still further, other than a radical polymerization, there can be also utilized an ion polymerization method and a group transfer polymerization method.

In the polymer (B0) to be employed in the present invention, a weight average molecular weight ranges in preferably 1000-100000 and,

particularly, preferably 3000-30000. Further, an isocyanate value appropriately ranges in 30-200 g/1000 g of a resin.

The polymer (B0) has at least two free isocyanate groups in the molecule and, preferably, it does not have at all an active hydrogen which can react with isocyanate group.

The polyol resin (A0): It is a resin having at least two hydroxyl groups in the molecule. Specifically, there are enumerated an acrylic resin (A0-1), a polyester resin (A0-2), and a fluorocarbon resin (A0-3), etc. which have at least two hydroxyl groups in the molecule, and all of the already-known products can be employed, provided that the polyol resin (A0) contains the above-described polyol resins (A) in a proportion of 0.5-80 parts by weight.

First of all, the acrylic resin (A0-1) is an acrylic-based resin having at least two hydroxyl groups in the molecule. The acrylic resin (A0-1) is a polymer which containing a monomer unit (hereinafter, referred to "hydroxyl group-contained monomer") having at least one of hydroxyl groups and at least one of radically-polymerizable double bonds, respectively, in the molecule as an essential component, and in which other vinyl monomers are further employed, and which does not contain the the NCO group-contained monomer.

As the hydroxyl group-contained monomer, for example, there are enumerated 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, hydroxybutylacrylate, 2,3-dihydroxypropyl acrylate, 2-hydroxy-3-phenoxyethylacrylate, and 2-hydroxy-3-ethoxyethylacrylate, etc. Further, there is enumerated an equimolar adduct of acrylic acid or methacrylic acid with a glycol

(a carbon number of 2-20), etc., a caprolactone-modified(meth)acrylate such as Placel FM-1, FM-2, FM-3, FM-4, FM-5, FA-1, FA-2, FA-3, FA-4, and FA-5 (which are manufactured by Daicel Chemical Industries, Ltd., a trade name, hereinafter, the same), and the hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones, in which a proportion of monomers having not less than 2 continuous chains ($n \geq 2$) of lactones is less than 50% of the present invention, etc. These may be also employed as a mixture of two or more kinds.

The other monomers, which can be copolymerized with the hydroxyl group-contained monomer, have a radically-polymerizable double bond in the molecule and, moreover, do not preferably contain an active hydrogen which can react with isocyanate group, specifically, there are preferred the vinyl monomers enumerated as other monomers in the illustration for the above-described vinyl polymer (B0).

Further, the acrylic resin (A0-1) is a resin essentially containing a (meth)acrylate (also including the hydroxyl group-contained monomer), etc., and the content thereof is preferably 20-100% by weight and, particularly, preferably 30-100% by weight in total monomers employed for the preparation of the acrylic resin (A0-1).

Construction ratio of the above-described monomers in the acrylic resin (A0-1) is not particularly limited, and the hydroxyl group-contained monomer is 1-100% by weight and, particularly, 10-60% by weight, a vinyl monomer having a carboxylate group is 0-20% by weight and, particularly, 0-5% by weight, and other vinyl monomers are 0-99% by weight and, particularly, preferably 40-90% by weight based on total weight of the monomer composition.

The acrylic resin (A0-1), as exemplified in the preparation of the polymer (A), can be obtained by a radical polymerization method using a polymerization initiator, a photo-polymerization method utilizing an electron beam or an ultraviolet ray, an ionic polymerization method, and a group transfer polymerization method,

As organic solvents to be employed in the polymerization methods, there is preferred an inert organic solvent not containing an active hydrogen which reacts with isocyanate group and, specifically, there are preferred the solvents exemplified in the item of the above-described block type isocyanate, and there are also preferred hydrophilic or water-soluble solvents not having an active hydrogen, for example, there are preferred diethyleneglycol dimethylether and ethyleneglycol dimethylether, etc.

On the other hand, in the case that the acrylic resin (A0-1) is synthesized in an organic solvent having an active hydrogen, it can be employed in a urethanation reaction with the polymer (A0) after removing the organic solvent under a reduced pressure or by condensing or spray drying.

In the acrylic resin (A0-1), a weight average molecular weight ranges in preferably 500-50000 and, particularly, preferably 2000-35000 and, hydroxyl group particularly appropriately ranges in 5-250 based on a hydroxyl value.

The polyester resin (A0-2) is a polyester-based resin having at least two hydroxyl groups in the molecule. The polyester resin (A0-2) is obtained by an esterification or transesterification reaction using

a polybasic acid having at least two carboxylic groups in the molecule and a polyvalent alcohol having at least two hydroxyl groups in the molecule as essential components and, optionally, using a fatty acid and/or a fatty acid ester as raw materials, so that free hydroxyl groups are contained.

As the polybasic acid and the polyvalent alcohol, for example, there are enumerated the polybasic acid and the polyvalent alcohol for the polyester polyols exemplified in the item of the block type isocyanate.

As the fatty acids, for example, there can be employed a (semi)drying oil fatty acid such as a safflower oil fatty acid, a linseed oil fatty acid, a soybean oil fatty acid, an eno oil fatty acid, a corn oil fatty acid, a tall oil fatty acid, a sunflower oil fatty acid, a cotton seed oil fatty acid, and a tung oil fatty acid; a coconut oil fatty acid; an olive oil fatty acid; and a palm oil fatty acid, etc. Of those, the (semi)drying oil fatty acid is preferably employed from a viewpoint of an improvement of properties in a coating layer.

In the polyester resin (A0-2), in general, an acid value (mgKOH/g of a resin) desirably ranges in not more than 200 and, preferably not more than approximately 100, and a hydroxyl value (mgKOH/g of a resin) ranges in approximately 5-400 and, preferably approximately 20-250. In the case that the hydroxyl value is less than approximately 5, curability in a coating layer lowers, and there is unpreferably observed a tendency of a decline of properties in a coating layer such as hardness and bending resistance and, on the other hand, in the case that the hydroxyl value becomes more than approximately 400, there is unpreferably observed a decline of properties in a coating layer such

as water resistance and corrosion resistance.

Introduction of hydroxyl groups into the polyester resin (A0-2) is preferably conducted by employing together a compound having at least three hydroxyl groups in the molecule, for example, as the polyvalent alcohol.

Further, in the polyester resin (A0-2), a weight average molecular weight ranges in generally approximately 500 to approximately 50000, and preferably approximately 1000 to approximately 30000 and, a softening point is not more than 150°C, and preferably not more than approximately 115°C.

The esterification reaction by respective components for the preparation of the polyester resin (A0-2) is preferably conducted under the presence of an organic solvent. As the organic solvent to be employed in the esterification reaction, there is preferred an inert organic solvent not having an active hydrogen which reacts with isocyanate group in consideration of an introduction of urethane bond derived from a urethane reaction with the vinyl polymer (B0) and, specifically, there are preferred the solvents exemplified in the item of the above-described block type isocyanate, and there are also preferred hydrophilic or water-soluble solvents not having an active hydrogen, for example, there are preferred diethyleneglycol dimethylether and ethyleneglycol dimethylether, etc.

On the other hand, in the case that the polyester resin (A0-2) having hydroxyl groups is synthesized in an organic solvent having an active hydrogen, it can be employed in a urethanation reaction with the polymer (B0) after removing the organic solvent under a reduced

pressure or by condensing or spray drying.

Further, as the polyester resin (A0-2) having hydroxyl groups, there can be also employed a ring-opened polymer of ϵ -caprolactone and, as a specific example thereof, there are enumerated Placel 208, 240, 305, and 308 which are manufactured by Daicel Chemical Industries, Ltd.

The fluorocarbon resin (A0-3) is a resin having at least two hydroxyl groups, and having fluorine atoms at a main structure or side chains.

The fluorocarbon resin (A0-3) is obtained by allowing to copolymerize partially or wholly employing a fluorine-contained polymerizable unsaturated monomer as other vinyl monomers which are occasionally employed for the preparation of the acrylic resin (A0-1) with the hydroxyl group-contained monomer.

As the fluorine-contained polymerizable unsaturated monomer, for example, there are enumerated a fluoroolefine represented by a general formula $CX_2=CX_2$ (in the formula, X may be identical to or different from each other, and represents H, Cl, Br, F, an alkyl group or haloalkyl group, provided that it contains at least one piece of F): a perfluoroalkyl(meth)acrylate such as a perfluorobutyl ethyl(meth)acrylate, a perfluoroisononyl ethyl(meth)acrylate, a perfluorooctyl ethyl(meth)acrylate, Viscose 3MF, Viscose 8F, Viscose 8MF, perfluorocyclohexyl(meth)acrylate, and N-2-propylperfluorooctane sulphonic amide ethyl(meth)acrylate, etc.

In the fluorocarbon resin (A0-3), properties such as a hydroxyl value and a weight average molecular weight may be nearly identical

to the above-mentioned acrylic resin (A0-1).

In the preparation of the self-crosslinkable resin (I), a reaction of the vinyl polymer (B0) with the polyol resin (A0) is a urethanation reaction of isocyanate group with hydroxyl group and, specifically, the urethanation reaction is conducted by formulating the polyol resin (A0) into an organic solution of the vinyl polymer (B0) at a temperature of usually 20-100°C, and preferably 25-60°C.

The reaction is controlled by the reduction amount of isocyanate group, that is, an isocyanate value. Further, in the reaction, a tin-based catalyst, etc. may be optionally even employed. Formulating amount of the polyol resin (A0) appropriately ranges in 0.1-10.0, and preferably 0.5-5.0 based on a functional group ratio in the vinyl polymer (B0) with respect to the polyol resin (A0), that is, NCO/OH ratio and, based on total weight of the both, the vinyl polymer (B0) ranges in 1-99% by weight, and preferably 10-70% by weight, the polyol resin (A0) ranges in 1-99% by weight, and preferably 30-90% by weight, provided that the polyol resin (A0) contains 0.5-80 parts by weight of the acrylic polyol resin (V-A) obtained using the hydroxyethyl(meth)acrylate composition modified by a small amount of lactones of the present invention with respect to 0.5-50 parts by weight of the polyisocyanate compound (V-B).

Further, formulation is conducted so that at least average 0.1 piece of urethane bond is introduced with respect to 1 molecule of the vinyl polymer (B0) having a weight average molecular weight of 500-50000, and preferably, average 0.5-1.5 piece of urethane bond is introduced with respect to 1 molecule of the vinyl polymer (B0) having

a weight average molecular weight of 500-30000 and, particularly, 1 piece of urethane bond is most preferably introduced with respect to 1 molecule of the vinyl polymer (B0).

Further, in the preparation of the self-crosslinkable resin (I), gelation in the reaction with the polyol resin (A0) can be prevented by employing the vinyl polymer (B0) containing m-isopropenyl- α , α' -dimethylbenzyl isocyanate having a tertiary isocyanate group as a vinyl polymer (B0), whereby, a coating layer can be preferably cured at a low temperature.

As described hereinabove, urethane bonds are introduced by allowing to react the polyol resin (A0) and, the self-crosslinkable resin (I) is obtained by completely blocking the residual free isocyanate group which is contained in the vinyl polymer (B0) in which the polyol resin (A0) is added through allowing to react with a blocking agent. As the blocking agent, for example, there are enumerated the compounds described hereinabove.

In principle, the blocking agent is preferably formulated in an amount to be required so as to react with all residual free isocyanate groups.

Reaction of a polymer in which the polyol resin (A0) is added with the blocking agent is usually conducted at a temperature of 20-100°C. Further, a tin-based catalyst may be even optionally employed.

The self-crosslinkable resin (II) is a self-crosslinkable resin simultaneously containing a block isocyanate group and hydroxyl group coexist in the molecule, and which is prepared by allowing to partially react hydroxyl groups in the polyol resin (A0) having at least two

hydroxyl groups with all the free isocyanate groups in a vinyl polymer (V-C) in which free isocyanate groups and block isocyanate groups coexist in the molecule.

The vinyl polymer (V-C) is a vinyl polymer simultaneously containing free isocyanate groups and block isocyanate groups coexist in the molecule and, specifically, it is obtained by allowing to partially react free isocyanate groups in the above-described vinyl polymer (B0) with a blocking agent. In relation to the vinyl polymer (B0) to be employed for the preparation of the vinyl polymer (V-C), as an NCO group-contained monomer, the above-described monomers can be employed and, particularly, there is preferred a vinyl polymer (B0) obtained by using an equimolar adduct of 2-isocyanate ethylmethacrylate, m-isopropenyl- α, α' -dimethylbenzyl isocyanate, and 2-hydroxyethylacrylate with isophorone diisocyanate.

Formulating amount of the blocking agent into the polymer may be an amount to be required for remaining the free isocyanate groups so that an introducing amount of urethane bonds derived from a reaction with the polyol resin (A0) in a succeeding step becomes a same level as in the above-described self-crosslinkable resin (I) and, particularly preferably, a reaction is preferably conducted by allowing to remain free isocyanate group being capable of introducing one piece of urethane bond per one molecule of the polymer (V-A) and by formulating an amount of the blocking agent to be required for completely blocking the remained free isocyanate.

And, the self-crosslinkable resin (II) is obtained by allowing to partially react hydroxyl groups in the polyol resin (A0) with all the remained free isocyanate in the polymer obtained by allowing to

react the blocking agent with a polymer. In other words, it is required that the amount of the hydroxyl groups in the resin (A0) is larger than the amount of the remained free isocyanate.

The reaction with the blocking agent for obtaining the self-crosslinkable resin (II) and the reaction of the polymer obtained with the resin (A0) are likewise conducted as illustrated in the self-crosslinkable resin (I).

In the self-crosslinkable resins (I) and (II), a molecule of a resin containing a block isocyanate group is connected to a molecule of the polyol resin through a urethane bond derived from a reaction of isocyanate group with hydroxyl group. Accordingly, those are also looked upon as a graft polymer by the both molecules.

Thus-obtained self-crosslinkable resins (I) and (II) have at least one piece of the block isocyanate group and one piece of hydroxyl group, and a weight average molecular weight is 1000-120000 or so and, particularly, preferably 5000-50000 or so.

In the self-crosslinkable resins to be employed in the present invention, crosslinking degree becomes highest as a self-crosslinkable coating layer by adjusting the amount of the block isocyanate group and hydroxyl group in the molecule to an equimolar amount, and hydroxyl group is preferably adjusted to an excessive amount in consideration of adhesion of a intermediate coating layer to a substrate and an over coating layer. In the resins, a hydroxyl value (mgKOH/g of a resin) appropriately ranges in 10-200, an isocyanate value (g/1000g of a resin) appropriately ranges in 15-150, and an acid value (mgKOH/g of a resin) appropriately ranges in not more than 200.

Coating in relation to the present invention contains the above-described curable resin composition as an essential component, and it is obtained by dissolving or dispersing the resin into an organic solvent or a water-based solvent and, optionally, there can be appropriately formulated a variety of additives which are conventionally employed in a coating field, for example, an ultraviolet ray absorbent, a photo-stabilizer, an antioxidant, a pigment for coloring, an extender pigment, a metallic pigment, an aluminum powder, a pearly mica powder, an anti-dropping agent or an anti-sedimentation agent, a leveling agent, a dispersant, a defoaming agent, an antistatic agent, a catalyst for curing, a flowability-adjusting agent, a cellulose acetate-butylate, and a thinner which are publicly- and commonly-known to prepare a two-liquid type coating or a single-liquid type coating composition.

Further, there can be employed other resins such as an epoxy resin and a polyester resin or a high molecular weight compound which has a good compatibility within a range in which an effect by the present invention is not decreased. Thus-obtained coating can be coated by publicly- and commonly-known methods such as spray coating, roller coating, and brush coating. It is to be noted that it goes without saying that the resin composition for a coating of the present invention can be employed as a clear coating in which pigments are not employed, or an enamel coating in which pigments are employed.

In the coating in relation to the present invention, there can be actualized a more exceedingly excellent acid resistance which does not include any practical problems compared to a coating prepared from a conventional polyol and melamine resin even though being further

employed together with other polyols and crosslinking agents (for example, a melamine resin). In the coating in relation to the present invention, in the case of simultaneously employing other polyol resins and melamine resins, the content of the curable resin composition of the present invention is not less than 10% by weight, and preferably not less than 25% by weight in total solid resin components, the content of the melamine resins are not more than 30% by weight, and preferably not less more than 20% by weight, in total solid resin components.

In the case that the curable resin composition of the present invention is less than 10% by weight or, the melamine resins are more than 30% by weight, an acid resistance cannot be unpreferably elevated.

As the melamine resins to be simultaneously employed, usual melamine resins for coatings can be employed without any modification, and imino type or methylol type melamine resins are employed. The imino type or methylol type melamine resins are not particularly limited in employing and, if those are resins to be employed for a coating-system in which hydroxyl group is employed as a functional group. As such the imino type melamine resins, for example, there are enumerated Yuban 22R (solid content of 60%), Yuban 21R (solid content of 50%), and Yuban 2028 (solid content of 75%) which are manufactured by Mitsui Kagaku (all of those are a imino type melamine resin), etc. On the other hand, as the methylol type melamine resins, there can be employed a melamine resin having a condensation degree of 1.1-20 or so which is prepared using melamine, formaldehyde, a monoalcohol of a carbon number of 1-4, and optionally water as raw materials. For example, there are enumerated Yuban 60R (solid content of 50%) manufactured by Mitsui Kagaku and Superbekkamine L-121-60 (solid content of 60%) manufactured by

Dainippon Ink Kagaku Kogyo, Ltd., etc.

As the polyol resins to be employed together with the curable resin composition of the present invention, for example, there are preferred the above-described acrylic resin (A0-1), polyester resin (A0-2), and fluorine resin (A0-3).

Provided, in the case of simultaneously employing the polyol resins, the polyol resins and the polyol resins (A0) definitively contain the acrylic polyol resin (V-A) in a proportion of 0.5-80 parts by weight with respect to 0.5-50 parts by weight of the polyisocyanate compound (V-B).

In the curable resin composition of the present invention, above all, in order to elevate weatherability such as retention of a gloss during exposure and a high extentionable property, there is preferably employed a mixture composed of an ultraviolet ray absorbent/hindered amine-based photo-stabilizer=(40-60)/(60-40) (ratio of solid components) within a range of 0-10 wt% based on solid components in the acrylic polyol resin (V-A). In the case that addition amount is not less than 10 wt%, since a price of a coating becomes expensive and, crystallines are occasionally formed at a low temperature and water resistance occasionally lowers, and a resin solution occasionally discolours, it is not preferred so much. Even in an outside value of the above mixing ratio of the ultraviolet ray absorbent with respect to the hindered amine-based photo-stabilizer, although an effective action is observed, the effective action is most excellently observed in a range of the above mixing ratio.

As typical examples of the ultraviolet ray absorbent, there can

be preferably employed benzophenone, 2,4-dihydrobenzophenone,
 2,2',4,4'-tetrahydroxy benzophenone,
 2-hydroxy-4-methoxybenzophenone,
 2,2'-dihydroxy-4,4'-dimethoxybenzophenone,
 2,2'-dihydroxybenzophenone, 2-hydroxy-4-octoxybenzophenone,
 2-hydroxy-4-dodecyloxybenzophenone,
 2-hydroxy-4-methoxy-5-sulphobenzophenone,
 5-chloro-2-hydroxybenzophenone,
 2,2'-dihydroxy-4,4'-dimethoxy-5-sulphobenzophenone,
 2-hydroxy-4-methoxy-2'-carboxybenzophenone, and
 2-hydroxy-4-(2-hydroxy-3-methyl-acryloxyisopropoxy)benzophenone;
 2-(2'-hydroxy-5-methyl-phenyl)-benzotriazole,
 2-(2-hydroxy-3,5-di-t-amyl-phenyl)-2H-benzotriazole,
 2-(2'-hydroxy-3',5'-di-t-butyl-phenyl)benzotriazole,
 2-(2'-hydroxy-3',5'-di-t-butyl-phenyl)-5-methyl-benzotriazole,
 2-(2'-hydroxy-3',5'-di-t-butyl-phenyl)-5-chloro-benzotriazole,
 2-(2'-hydroxy-3',5'-di-t-isoamyl-phenyl)benzotriazole, and
 (2-hydroxy-5-t-butyl-phenyl)benzotriazole; phenylsalicylate,
 4-t-butyl-phenylsalicylate, and p-octyl-phenylsalicylate;
 ethyl-2-cyano-3,3'-diphenylacrylate,
 2-ethylhexyl-2-cyano-3,3'-diphenylacrylate;
 hydroxy-5-methoxy-acetophenone, 2-hydroxy-naphtophenone;
 2-ethoxyethyl-p-methoxycinnamate; nickel-bis-octylphenylsulphide;
 and anilide oxalate, etc., for example, a benzotriazole-based
 ultraviolet ray absorbent such as Tinuvin 900, Tinuvin 383, and Tinuvin
 P (manufactured by Ciba Geigy), an anilide oxalate-based ultraviolet
 ray absorbent such as Sandbar 3206 (manufactured by Sand), etc. A fixed

amount of the absorbents may be added in a terminating period of a copolymerization reaction of the acrylic polyol or in the preparation of a coating. On the other hand, in the case of T-17, T-37, and T-38 (all of those are a product by Adeka Argus Kagaku, Ltd.) which are a reactive ultraviolet ray absorbent containing an organic group having an ultraviolet ray absorbing ability such as an O-hydroxybenzophenone group and an ethylenic copolymerizable unsaturated bond such as methacrylic acid group in an identical molecule, a fixed amount thereof may be simultaneously introduced by copolymerizing at a copolymerization step of the acrylic polyol resin (A) components.

As examples of the hindered amine-based photo-stabilizer, there can be preferably employed a piperidine-based one which is usually called HALS (HALS) and typically includes 4-benzoyloxy-2,2,6,6-tetramethylpiperidine, bis(2,2,6,6-tetramethyl-4-piperidine)sebacate, or Tinuvin 144, 292, and 765 (all of those are a product manufactured by Ciba Geigy, A.G.), MARK LA-57, 62, 63, 67, and 68 (all of those are a product by Adeka Argus Kagaku, Ltd.), Sanol LS292 (manufactured by Sankyo), and Sandbar 3058 (manufactured by Sand). A fixed amount of the stabilizers may be added in a terminating period of a copolymerization reaction of the acrylic polyol resin (A) or in the preparation of a coating. In the case of a hindered amine-based compound containing an organic group having a photo-stabilizing ability and an ethylenic copolymerizable unsaturated bond such as (meth)acrylic acid group such as the MARK LA-82, 87, and T-41 (all of those are a product by Adeka Argus Kagaku, Ltd.), a fixed amount thereof may be simultaneously introduced by copolymerizing at a synthesis step of the acrylic polyol resin (A)

components.

Further, in order to increase an effectiveness thereof, optionally, there can be simultaneously employed an antioxidant such as "Sumilizer BHT" (a product manufactured by Sumitomo Kagaku Kogyo, Ltd.), "Seenox BCS" (a product manufactured by Shiroishi Calcium, Ltd.), "Irganox 1010 or 1076" (a product manufactured by Ciba Geigy, A.G.), "Noclizer TNP" (a product manufactured by Ohuchi Shinko, Ltd.), and "Antioxidant KB" (a product manufactured by West Germany/Bayer. A.G.), which are well known and commonly-used.

As the catalysts for curing, there are enumerated a phosphate, an organic acid such as dodecylbenzene sulphonic acid or paratoluene sulphonic acid and an amine acid thereof, an organic tin compound such as dibutyltin dilaurate and dibutyltin maleate and a chelating compound thereof, etc.

As the coloring pigments, extender pigments, leveling agents, dispersants, defoaming agents, photostabilizers, thinners, and antistatic agents, for example, there are enumerated ones exemplified in the above-described present invention III.

In the case of preparing a coating composition using the curable resin composition of the present invention, there are mixed the acrylic polyol resin (V-A), the polyisocyanate compound (V-B), and optionally, additives such as acidic-dissociation catalysts and pigments, and uniformly dispersed by a dispersing machine such as a sand grind mill, a ball mill, and a tlighter to prepare a curable type coating composition.

Coating of the coating composition obtained as described hereinabove may be conducted according to the methods illustrated in

the present invention III.

VI.

Hereinafter, the present invention VI is illustrated.

The present invention VI is a curable resin composition comprising an acrylic polyol resin (VI-A) obtained by using a hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones, in which a proportion of monomers having not less than 2 continuous chains ($n \geq 2$) of lactones represented by the general formula (1) is less than 50% (GPC area %), and a polyisocyanate compound (VI-B).

The hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones to be employed in the present invention is as illustrated in the present invention I.

By allowing to polymerize alone the hydroxyalkyl (meth)acrylate composition (a) modified by a small amount of lactones to be employed in the present invention or by allowing to copolymerize with other radically-polymerizable monomers, there can be provided a curable acrylic polyol which is excellent in reactivity with a crosslinking agent and rich in flexibility, and it can be utilized as a material for the curable resin composition for coating of the present invention.

In the present invention, the other radically-polymerizable monomers are employed to copolymerize with the lactone-modified (meth)acrylate having hydroxyl group. The acrylic polyol resin (VI-A) in relation to the present invention is a vinyl copolymer having carboxylic group and a crosslinkable functional group, which is obtained by allowing to react a hydroxyalkyl(meth)acrylate composition (a) modified by small amount of lactones with a vinyl monomer having

carboxylic group and other vinyl-based monomers.

As the vinyl-based monomer having carboxylic group to be employed in the present invention, only particularly typical examples are exemplified, and which include an α, β -ethylenic unsaturated carboxylic acid such as acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid (anhydride) or fumaric acid (anhydride), itaconic acid, itaconic anhydride, and citraconic acid.

As the other vinyl-based monomer, there are enumerated a polymerizable vinyl monomer containing an active hydrogen and other polymerizable unsaturated monomers, and the following compounds are exemplified.

As a (meth)acrylate, for example, an alkyl or cycloalkyl ester having a carbon number of 1-20 of a (meth)acrylic acid such as methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, isopropyl(meth)acrylate, butyl(meth)acrylate, hexyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, octyl(meth)acrylate, lauryl(meth)acrylate, tridecyl(meth)acrylate, stearyl(meth)acrylate, cyclohexyl(meth)acrylate, isobonyl(meth)acrylate, and adamantyl(meth)acrylate; a (meth)acrylate such as benzyl(meth)acrylate; an alkoxyalkyl ester having a carbon number of 2-8 of a (meth)acrylic acid such as methoxybutyl(meth)acrylate, methoxyethyl(meth)acrylate, and ethoxybutyl(meth)acrylate; a fluorine-contained vinyl monomer such as Viscose 3F, 3MF, 8F, and 8MF (manufactured by Osaka Yuki Kagaku, Ltd., a trade name), perfluorocyclohexyl(meth)acrylate, N-2-propylperfluoro octane sulphonic amide ethyl(meth)acrylate, vinylfluoride, and vinylidene fluoride; a nitrogen-contained vinyl monomer such as

N,N'-diethylaminoethyl(meth)acrylate,
N,N'-diethylaminoethyl(meth)acrylate, N,N'-diethylaminoethyl
(meth)acrylate, and N,N'-diethyl(meth)acrylic amide; a
vinylether-based monomer such as vinylethylether and vinylbutylether;
and glycidyl(meth)acrylate,
3,4-epoxycyclohexylmethyl(meth)acrylate, an alkyletherized compound
such as arylglycidyl ether and methylol acrylic amide, (meth)acrylic
amide, (meth)acrylic chloride, vinylchloride, vinylidenechloride,
(meth)acrylonitrile, and γ -methacryloxyalkyl trimethoxy silane, an
aromatic vinyl monomer such as styrene, α -methylstyrene, and
vinyltoluene; (meth)acrolein, butadiene, isoprene, methylisopropenyl
ketone, etc., and these are employed solely or as a mixture of two
or more kinds.

As the polymerizable monomer having an active hydrogen, there
are enumerated a (meth)acrylate having hydroxyl group described below
and a (meth)acrylate having amino group, these can be employed in mixing.

As the (meth)acrylate having hydroxyl group, for example, there
are enumerated hydroxyalkyl(meth)acrylates having a carbon number of
2-8 such as hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate,
hydroxybutylacrylate, 2,3-dihydroxypropylacrylate,
2-hydroxy-3-ethoxyethylacrylate, 2-hydroxy-3-ethoxyethylacrylate,
etc., an equimolar adduct of acrylic acid or methacrylic acid with
a glycol (a carbon number of 2-20), etc., and a
caprolactone-modified(meth)acrylate such as Placel FM-1, FM-2, FM-3,
FM-4, FM-5, FA-1, FA-2, FA-3, FA-4, and FA-5 (manufactured by Daicel
Chemical Industries, Ltd., a trade name).

These may be also employed as a mixture of two or more kinds.

As the (meth)acrylate having amino group, there are enumerated aminoalkyl(meth)acrylates such as dimethylaminoethyl (meth)acrylate and diethylaminoethyl(meth)acrylate; and a (meth)acryl amide, etc., those can be employed solely or in mixing of two or more kinds.

The above-described other vinyl monomers can be also employed in mixing, and can be selected according to a desired physical property.

The acrylic polyol resin (V-A) to be employed in the present invention is prepared by radically-polymerizing under the presence of a radical polymerization initiator by publicly-known solution polymerization methods.

As the radical polymerization initiator, there can be employed a peroxide initiator such as benzoyl peroxide, t-butylhydroperoxide, cumylhydroperoxide, cumenhydroperoxide, t-butyl peroxybenzoate, and t-butylperoxy-2-ethylhexanoate, and an azo-based initiator such as azobisisobutyronitrile and azobisdimethylvaleronitrile.

As solvents to be employed in the solution polymerization, for example, there are enumerated aromatic hydrocarbons such as benzene, toluene, and xylene; ester-based ones such as ethyl acetate, propyl acetate, butyl acetate, and cellosolve acetate; ether-based ones such as dioxane, and ethylene glycol dibutylether; ketones such as acetone, methylethylketone, and methyl isobutyl ketone. The solvents may be employed solely or in combination of two or more kinds.

As a reaction vessel to be employed for the above-described polymerization, there is preferably employed a reaction vessel equipped with an agitation and a reflux condenser equipped with a drying tube, and a twin-screw extruder.

Polymerization temperature and polymerization time of period depend upon respective kinds and feeding ratio of the hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones of the present invention, the above-described vinyl-based monomer having carboxylic group, the above-described other vinyl-based monomer, a kind and an amount of the catalysts, reaction apparatuses, and those are not particularly limited, and those are appropriately decided by the use of a desired curable oligomers or (co)polymerized acrylic resins, and physical properties of a coating layer in the case of a coating. Such the polymerization reaction is conducted at a temperature of 60-150°C or so using the usual radical polymerization initiator in the organic solvents.

In the acrylic polyol resin (VI-A) to be employed in the present invention, since there can be readily designed a molecular weight, composition, and a structure, and it is excellent in weatherability, it can provide novel crosslinked particles which can be applied in wide uses which require corrosion resistance.

In the resin having hydroxyl group to be employed in the present invention, content of hydroxyl group is preferably not less than 10 as a hydroxyl value and, in the case that the hydroxyl value is less than 10, vinyl groups are not sufficiently introduced, and it becomes difficult to copolymerize with a variety of polymerizable monomers including the polymerizable monomers having carboxylic group, resulting in that a water dispersion property often lowers.

Further, there becomes insufficient a reaction with the polyisocyanate compound (V-B) (a hydrophobic crosslinking agent) and, as a result, a sufficient corrosion resistance cannot be obtained by

a decline of crosslinking degree.

On the other hand, although the copolymer which becomes a hydrophobic portion may even contain acidic components, in the case, an acid value is desirably not more than 10. In the case containing more than 10 of such the acidic components, a hydrophilic property is unavoidably elevated and a core-shell structure is destroyed, resulting in that stability lowers after introduction of a hydrophobic crosslinking agent.

Further, in the acrylic polyol resin (VI-A) to be employed in the present invention, a number average molecular weight appropriately ranges in 3,000-100,000. It preferably ranges in 3,000-50,000. In the case that the number average molecular weight is less than 3,000, since it becomes impossible to stably introduce the polyisocyanate compound (V-B) (a hydrophobic crosslinking agent) into the particles and, further, since there are not occasionally obtained physical properties in a coating layer such as sufficient water resistance and outer appearance of a coating layer, it is not preferred.

On the other hand, in the case that the number average molecular weight is more than 100,000, gelation is unavoidably caused, otherwise, viscosity largely increases during emulsifying by a phase inversion, resulting in that it unpreferably becomes difficult to produce an excellent water-dispersion.

Further, it is also required that content of the vinyl-based monomers having carboxylic group which becomes a hydrophilic segment is at least 10 of an acid value as a minimum limit for self-emulsifying of a resin.

Herein, although carboxylic group is employed as the hydrophilic segment, since a sufficient hydrophilic property is not shown in the case of a state of a carboxylic acid, usually, it is preferred that the hydrophilic property is increased by a change to an amine salt.

Even in the case that the content of carboxylic group is of a large amount, if a carboxylic acid salt neutralized by an amine salt is of a small amount, a resin does not manifest a self-emulsifying property. That is, if a neutralization ratio by the amine salt is excessively high, even in the case that it becomes water-soluble, a water-dispersible resin becomes obtained by decreasing the neutralization ratio. However, even though 100% of carboxylic groups contained in view of composition are neutralized, it should be designed so that it does not become water-soluble.

Further, since the carboxylic group itself is high in polarity, in the case that the content exceeds 60% by weight, it is not preferred because of adversely affecting to corrosion resistance.

As content of the hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones of the present invention, it requires not less than 10 as a hydroxyl value in the vinyl-based copolymer obtained in consideration of a reaction with the crosslinking agent.

However, in the case of a resin in which the content of the hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones of the present invention exceeds 300 as a hydroxyl value, such the content is not preferred because of adversely affecting to a corrosion resistance.

The acrylic polyol resin (VI-A) in relation to the present

invention may be even a vinyl-based copolymer having carboxylic groups and crosslinkable functional groups which is obtained by allowing to react a resin having hydroxyl groups obtained by polymerization of the hydroxyakyl(meth)acrylate composition modified by a small amount of lactones with (meth)acrylic anhydride, and then allowing to react a reaction product obtained with the above-described vinyl-based monomer having carboxylic group and the above-described other vinyl-based monomers.

Further, the acrylic polyol resin (VI-A) in relation to the present invention may be even a resin having hydroxyl groups obtained by using the above-described resin having hydroxyl groups and at least one of resins selected from the group consisting of the above-described resin having hydroxyl groups, urethane resin having hydroxyl groups, epoxy resin having hydroxyl groups, cellulose derivative having hydroxyl groups, and polyester resin having hydroxyl groups.

In the case, as the resin having hydroxyl groups, there should be employed a hydrophobic resin not having a self-water dispersible property. Vinyl group can be readily introduced by allowing to react such the hydrophobic resin not having a self-water dispersible property with a specified acid anhydride such as (meth)acrylic anhydride.

The kind of copolymers form core-shell structure type particles in which a hydrophobic portion and hydrophilic portion are differently separated from each other. For that reason, there can be formed crosslinked particles which are particularly excellent in a dispersion stability after introduction of the polyisocyanate compound (V-B) (a hydrophobic crosslinking agent).

Further, such the copolymers cannot be modified to a water-soluble

resin because of forming a core-shell structure after emulsifying by a phase inversion in spite of a high neutralization ratio in carboxylic groups. In other words, it may safely be said that it is a resin which is excellent in capability of accepting a hydrophobic substance such as the hydrophobic crosslinking agent.

Still further, such the resin having hydroxyl groups can be also employed together with a condensation-based resin without being limited to a radical polymerization-based resin.

It has a merit of capability of selecting an appropriate resin according to various grade of corrosion resistance to be desired or various uses and capability of employing together. In addition, it may safely be said that there has been certainly conventionally nothing in a method for readily preparing the crosslinked particles using a variety of the condensation-based resins.

By using the crosslinked particles having such a novel structure, for the first time, there can be provided a novel and useful coating which is excellent in corrosion resistance.

Incidentally, glycidyl groups can be also allowed to copolymerize with the resin having hydroxyl group. Such the glycidyl groups are contained in the core portion of a particle after emulsifying by a phase inversion and, whereby, the groups are isolated from carboxylic groups contained in adjacent particles and, as described above, in the case that glycidyl groups are allowed to copolymerize with the vinyl-based resin having hydroxyl group, there can be obtained exceedingly good crosslinked particles which are excellent in a

dispersion stability (in more detail, gelation is not caused after a time lapse).

Glycidyl groups act in order to elevate a crosslinking degree by partially reacting with the carboxylic groups contained in the polyisocyanate compound (V-B) (a hydrophobic crosslinking agent) or in a copolymer which forms the core portion after formation of particles.

Further, the glycidyl groups remained in the core portion act also as functional group for self-crosslinking in the crosslinked particles themselves during baking.

In a water-based coating, a high molecular weight type epoxy resin can be simultaneously employed and, if such a method is applied, there can be also employed a low molecular weight epoxy resin such as "Epikote 1001" [a product by Dainippon Ink Kagaku Kogyo, Ltd.], provided that it is desirably employed in a field in which weatherability is not required.

As the aromatic epoxy resins to be employed, for example, there are enumerated a bisphenol A type epoxy resin, a bisphenol F type epoxy resin, and a novolak type epoxy resin, etc.

Of the epoxy resins, there is desired an epoxy resin having an epoxy equivalent of not less than 400, and there is also preferably employed an epoxy resin having an epoxy equivalent of not less than 4,000.

As an epoxy resin having an epoxy equivalent of 400-4,000, for example, there are enumerated "Epikote 1001, 1004, 1007 or 1009" manufactured by Shell, A.G. in Netherlands, or "Epichlone 4055, 7055, and 9055" manufactured by Dainippon Ink Kagaku Kogyo, Ltd., etc.

Further, as an epoxy resin having an epoxy equivalent of not less than 4,000, for example, there are enumerated "Epikote 1010 or 1100L" manufactured by Shell, A.G., or "PKHA", "PKHC", "PKHH", or "PKHJ" which are a phenoxy resin manufactured by Union Carbide, Co. in USA.

Still further, as the epoxy resin, in addition to the above-described ones, there can be also employed a variety of modified epoxy resins such as a fatty acid-modified epoxy resin, a phenol-based compound-modified epoxy resin, or an alcohol-based compound-modified epoxy resin.

As the fatty acids to be employed for modifying, there are enumerated a variety of vegetable oil fatty acids such as a soybean oil fatty acid or a castor oil fatty acid; a variety of organic acids such as benzoic acid or acetic acid and, as the phenol-based compound, there are enumerated bisphenol A, phenol, and cresol, etc. and, further, as the alcohol-based compound, there are enumerated methanol, butanol, or benzyl alcohol, etc. By heating these modifiers with aromatic-based epoxy resin at 100-170°C or so under the absence or the presence of appropriate reaction catalysts such as a tertiary amine or a quaternary amine, the above-described epoxy resins are obtained.

It is needless to say that there can be employed solely the respective groups of epoxy resins or a plurality of epoxy resins in the respective groups, or there can be (simultaneously) employed a plurality of epoxy resins between the respective groups.

Further, cellulose derivatives having hydroxyl groups can be also simultaneously employed. Such the cellulose derivatives are a resin system which is excellent in, particularly, oil resistance and solvent resistance, and there are obtained crosslinked particles which are

different in characteristics from the above-described vinyl-based resin having hydroxyl group in such a viewpoint.

However, in the case that the cellulose derivatives are employed in a water-based coating, since hydrolysis resistance and thermally-yellowing resistance are low and uses are occasionally limited, it must be paid attention to.

As the cellulose derivatives having hydroxyl groups, there is typically enumerated, for example, an ester-modified cellulose derivatives having hydroxyl groups or an ether-modified cellulose derivatives having hydroxyl groups, which is usually for a coating.

First, if there are typically exemplified only the ester-modified cellulose derivatives having hydroxyl groups, there are enumerated a nitrocellulose, a cellulose acetate-butylate, a cellulose acetate-propionate, a cellulose acetate-phthalate, an acetyl cellulose, a cellulose propionate, a cellulose butylate, a cellulose phosphate, and a cellulose sulphate, etc.

Further, if there are typically exemplified only the ether-modified cellulose derivatives having hydroxyl groups, there are enumerated a methyl cellulose, an ethyl cellulose, a butyl cellulose, a benzyl cellulose, a carboxymethyl cellulose, a carboxyethyl cellulose, an aminoethyl cellulose, an oxyethyl cellulose, a hydroxyethyl cellulose, a hydroxypropyl cellulose, and a hydroxypropyl methyl cellulose, etc.

Of the cellulose derivatives having hydroxyl groups, there is particularly desired the use of the cellulose acetate-butylate (hereinafter, it is referred to as CAB) obtained by further butyl-esterifying a partially acetylated cellulose.

In the cellulose derivatives having hydroxyl groups to be employed in the present invention, a number average molecular weight preferably ranges in 3,000-300,000, and more preferably in 5,000-150,000.

Further, in the cellulose derivatives having hydroxyl groups, content of hydroxyl groups is desirably not less than 0.4% by weight. In the case that the content of hydroxyl groups is less than 0.4% by weight, a grafting ratio lowers because (meth)acryloyl groups becomes unavoidably slight which are introduced into the cellulose derivatives having hydroxyl groups, unpreferably resulting in that the modified polymer having carboxylic groups is not apt to be self-emulsified.

If there are typically exemplified only the cellulose derivatives having hydroxyl groups as commercially supplied products, there are enumerated "CAB" series, "CAP" series, and "CA" series which are manufactured by Eastman Kodak, Ltd. in USA.

Further, a urethane resin having hydroxyl groups can be also simultaneously employed. By the use of the urethane resin, there can be obtained characteristics such as elasticity and flexibility derived from the urethane resin, and there can become obtained a coating layer having a corrosion resistance which is tough in impact.

Such the polyurethane resin having hydroxyl groups is obtained by allowing to polymerize an aliphatic and/or cycloaliphatic diisocyanate with an alkyl diol, a polyether diol, a polyester diol, or a mixture thereof and, optionally, a low molecular weight polyhydroxy compound under the presence or absence of an organic solvent not containing an active hydrogen atom (an active hydrogen group) in the molecule in a proportion of OH/NCO equivalent ratio ranging in 1.1-1.9

by a one-shot method or a multi-stage method.

Herein, in the case that the OH/NCO equivalent ratio is less than 1.1, hydroxyl value becomes unavoidably small, resulting in that introduction of vinyl group is apt to become insufficient and, as a result therefrom, copolymerization with a monomer having carboxylic group described later is apt to become insufficient and, as a result, a water dispersion property often lowers.

On the other hand, in the case of exceeding 1.9, products having low molecular weight are unavoidably produced, and there become unpreferably observed various characteristics such as physical properties in a coating layer.

As the above-described aliphatic and cycloaliphatic diisocyanate to be employed for the preparation of such the polyurethane resin having hydroxyl groups, particularly, there are typically enumerated aliphatic diisocyanates having a carbon number of 2-12 such as hexamethylene diisocyanate, 2,2,4-trimethylhexane diisocyanate, or isophorone diisocyanate, and particularly, there are typically enumerated cycloaliphatic diisocyanates having a carbon number of 4-18 such as 1,4-cyclohexane diisocyanate, 1-isocyanate-3-isocyanatemethyl-3,5,5-trimethylcyclohexane (isophorone diisocyanate), 4,4'-dicyclohexylmethane diisocyanate, methylcyclohexylene diisocyanate, and isopropylidene dicyclohexyl-4,4'-diisocyanate.

Further, there can be enumerated a modified product (carbodiimide, urethodion or urethoimine-contained modified product) of the various diisocyanates, or a mixture of two or more kinds.

Of those, as a preferred one, there are enumerated the

cycloaliphatic diisocyanates, particularly, 1,4-cyclohexane diisocyanate,

1-isocyanate-3-isocyanatemethyl-3,5,5-trimethylcyclohexane or 4,4'-dicyclohexylmethane diisocyanate.

Herein, in the case that an aromatic diisocyanate is employed, a coating layer is apt to yellow in curing for baking and, since the coating layer is apt to discolor by an influence of an ultraviolet ray, there must be paid attention according to uses.

As the polyetherdiol, there are particularly exemplified typical examples alone, and there are enumerated a variety of alkylene oxides such as ethyleneoxide, propylene oxide, or butylene oxide; a compound obtained by polymerization or copolymerization of a variety of heterocyclic ethers such as tetrahydrofuran; or a polyethylene glycol, a polypropylene glycol, a polyethylene-polypropylene glycol, a polytetramethylene etherglycol, and a polyhexamethylene etherglycol, etc.

As the polyesterdiol, there are particularly exemplified typical examples alone, and there are enumerated compounds such as a polyethylene adipate, a polybutylene adipate, a polyhexamethylene adipate, a polyneopentyl adipate, a poly-3-methylpentyl adipate, a polyethylene/polybutylene adipate, a polyneopentyl/hexyl adipate which are obtained by polycondensation of dicarboxylic acids typified by adipic acid, succinic acid, sebasic acid, maleic acid, fumaric acid, and phthalic acid with glycols typified by ethylene glycol, propylene glycol, 1,4-butane diol, 1,6-hexane diol, 3-methyl-1,5-pentane diol, neopentyl glycol, bishydroxymethyl cyclohexane; or polylactone diols

typified by a polycaprolactone diol, a poly-3-methyl-valerolactone diol; polycarbonate diols; or a mixture of two or more kinds thereof, etc.

As the alkyldiol, there are particularly exemplified typical examples alone, and there are enumerated fatty acid esters of glycerine.

Further, as polyhydroxy compounds having a low molecular weight, there are particularly exemplified typical examples alone, and there are enumerated glycols having a number average molecular weight of less than 500 which are enumerated as raw materials for the polyester diols or adducts (a molecular weight of less than 500) in which a small amount of an alkylene oxide is added to the glycols; a variety of trivalent alcohols such as glycerine or trimethylol propane, or adducts (a molecular weight of less than 500) in which a small amount of an alkylene oxide is added to the trivalent alcohols; and a mixture of two or more kinds thereof, etc.

Amount of the polyhydroxy compounds having a low molecular weight appropriately ranges in usually 0.1-20% by weight, and preferably 0.5-10% by weight with respect to the above-described polyether diols or polyester diols.

Further, as polyether diols and/or polyester diols to be employed for the preparation of the above-described urethane resins, there are employed ones having a number average molecular weight of 500-5,000, and preferably 1,000-3,000.

In the case that the number average molecular weight is less than 500, the urethane resins unavoidably becomes rigid, resulting in that desired properties are not obtained in a coating layer and, on the

other hand, in the case of excessively exceeding 5,000, a molecular weight in the urethane resins obtained also becomes high and, as a result, a hydroxyl value lowers, resulting in that a modification by a vinyl becomes insufficient.

Further, as described later, it is needless to say that carboxylic groups may be introduced for the purpose of elevating compatibility with a copolymer from a variety of polymerizable monomers including a variety of carboxylic group-contained polymerizable monomers, and adhesion to a body to be covered (a body to be coated). Specifically, for example, it is introduced by allowing to react a variety of dimethylol alkane acids such as dimethylol propionic acid.

However, the introduction of hydrophilic groups such as carboxylic groups elevates a hydrophilicity in the urethane resins and, as a result therefrom, since water resistance is lowered in a coating layer, addition amount is preferably limited to not more than 5% by weight.

Likewise, although the polyester-based resin can be also employed together as a resin having hydroxyl groups, a small molecular weight causes a problem of hydrolysis resistance in the case of a water-based coating. On the other hand, since a large molecular weight occasionally causes an insufficient modification and an amount of crosslinkable functional groups becomes insufficient, crosslinking density cannot be elevated. For that reason, there is observed a tendency of poor solvent resistance.

As described hereinabove, a variety of resins having hydroxyl groups are allowed to react with (meth)acrylic anhydride in an inert organic solvent under the absence of catalysts and, moreover, at a

relatively low temperature of 60-80°C for 1-6 hours or so while agitating to introduce vinyl groups in to the resins.

A reaction (esterification) in the case is conducted by monitoring with, for example, a Fourier transformation ultraviolet ray photometer (FI-IR) until an absorption by a specified acid anhydride such as (meth)acrylic anhydride is not observed or maintained at a low constant value, whereby, completion of the reaction can be confirmed through such means or methods. It is to be noted that a confirmation means is not limited thereto alone.

In the present invention, as the inert organic solvent to be employed in synthesis of the resin having hydroxyl groups and the reaction with an anhydride, there are particularly exemplified typical examples alone, and there are enumerated a variety of ketones such as acetone, methylethyl ketone, methylisobutyl ketone, ethylpropyl ketone, and ethylbutyl ketone; esters; or aromatic hydrocarbons, etc., and those are preferably employed.

The (meth)acrylic anhydrides are allowed to react in a proportion of an amount to be modified by the (meth)acrylic anhydrides of 0.5-30% with respect to hydroxyl group equivalent contained in 100 g of the resin having hydroxyl groups. In the case that the amount to be modified is less than 0.5%, vinyl groups are not sufficiently introduced, resulting in that copolymerization with monomers, which is successively conducted, is not sufficiently conducted and a water dispersion property lowers.

On the other hand, in the case of exceeding 30%, those are highly-polymerized by successive copolymerization, and gelation is

unpreferably apt to be caused.

By allowing to react the vinyl group-modified resin having hydroxyl groups obtained herein with a variety of vinyl-based monomers including a carboxylic group-contained vinyl-based monomer as an essential component, the acrylic polyol resin (VI-A) is obtained which is a desired product.

Incidentally, in the case of obtaining the acrylic polyol resin (VI-A), there can be also blended two or more kinds of the vinyl group-modified resin having hydroxyl groups.

For example, in the resin having hydroxyl groups, a crosslinking density can be also controlled by blending a copolymer having glycidyl groups with a copolymer not having glycidyl groups obtained by homopolymerizing or copolymerizing the hydroxyakyl(meth)acrylate composition modified by a small amount of lactones in relation to the present invention.

In the case, since a crosslinking agent and glycidyl groups form a crosslinked structure like an IPN (Interpenetrating polymer network), respectively, there is shown a more excellent corrosion resistance.

Further, by blending the resin having hydroxyl groups with the urethane resin having hydroxyl groups, there can be also conveniently achieved flexibility in a urethane resin and preparation of a vinyl-based polymer.

In the case, even in different kind of resins themselves, since those are partially connected by chemical bonds through simultaneously copolymerizing those, compatibility becomes excellent, and clouding, etc. in a coating layer is not apt to be caused.

As polymerizable monomers to be (co)polymerized with the vinyl

group-modified resins having hydroxyl groups, there are basically employed monomers containing at least 10% by weight of the vinyl-based monomer having carboxylic group in total polymerizable monomers. In the case that use amount of the vinyl-based monomer having carboxylic group is less than 10% by weight, there is unpreferably observed a tendency that dispersion stability of a resin becomes unavoidably worse in a water-based medium.

For example, as the vinyl-based monomer having carboxylic group and other vinyl-based monomers, the above-mentioned ones are enumerated. Incidentally, as a reaction ratio of the vinyl group-modified resins having hydroxyl groups with respect to a variety of the vinyl-based monomers having carboxylic group, ratio of the former resins:latter monomers appropriately ranges in 20:80-90:10 by weight ratio.

In the case that the use ratio of the vinyl-modified resins having hydroxyl groups is less than 20% by weight, since there is occasionally observed a case that a variety of properties in a resin are not unavoidably made the most, it is not preferred and, on the other hand, in the case that the use ratio of the resins is more than 90% by weight, the number of carboxylic groups becomes small, and a self-dispersion property becomes insufficient in a resin obtained, unpreferably resulting in that dispersing becomes often impossible in a water-based medium.

There is conducted a polymerization reaction of a variety of the vinyl-based monomers including the carboxylic group-contained vinyl-based monomer with the vinyl-modified resins having hydroxyl groups using a variety of radical polymerization initiators such as azobisisobutyronitrile or benzoyl peroxide which are publicly-known

at a temperature of 60-150°C or so in an inert organic solvent.

As the organic solvent in the case of conducting the reaction, there are particularly exemplified typical examples alone, there are enumerated a variety of ketones such as acetone, methylethyl ketone, and diisobutyl ketone; or aromatic hydrocarbons such as toluene or xylene. Further, there can be also preferably employed a variety of ester-based solvents such as ethyl acetate or butyl acetate.

In a method for the preparation of crosslinked particles in the present invention, a variety of the acrylic polyols (VI-A) (a self-dispersible crosslinking agent) as described hereinabove are mixed with the polyisocyanate compound (VI-B) (a hydrophobic crosslinking agent), and then, emulsified by phase inversion into a water-based medium to involve the hydrophobic crosslinking agent in the particles, followed by accelerating crosslinking in the particles, whereby, desired crosslinked particles can be obtained.

As the polyisocyanate compound (VI-B) to be employed in the present invention, there are aromatic, aliphatic, and cycloaliphatic polyisocyanates and, as the aromatic polyisocyanates, there are preferred polyisocyanates having a carbon number of 6-30, as the aliphatic polyisocyanates, there are preferred polyisocyanates having a carbon number of 4-30, and as the cycloaliphatic polyisocyanates, there are preferred polyisocyanates having a carbon number of 8-30. For example, there are enumerated 2,4-naphthalene diisocyanate, 1,5-naphthalene diisocyanate, 4,4'-diphenylmethane diisocyanate, 4,4'-diphenyldimethylmethane diisocyanate, dialkyldiphenylmethane diisocyanate, tetraalkyldiphenylmethane diisocyanate,

4,4'-diphenylene diisocyanate, 4,4'-dibenzyl diisocyanate, 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, tolylene diisocyanate such as 2,4-tolylene diisocyanate and, 2,6-tolylene diisocyanate, xylilene diisocyanate such as p-xylilene diisocyanate and m-xylilene diisocyanate, 1,4-tetramethylene diisocyanate, 1,5-pentamethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethylhexamethylene-1,6-diisocyanate, 2,4,4-trimethylhexamethylene-1,6-diisocyanate, ridine diisocyanate, cyclohexane-1,4-diisocyanate, isophorone diisocyanate, 4,4'-diisocyanate dicyclohexane, dicyclohexylmethane-4,4'-diisocyanate, methylcyclohexane diisocyanate such as 1,3-bis(isocyanatemethyl)cyclohexane and methylcyclohexane-2,4 (or 2,6)-diisocyanate, or an adduct of these diisocyanates to a polyvalent alcohol such as ethyleneglycol, propylene glycol, a polyethylene glycol, a polypropylene glycol, a polycaprolactone polyol, trimethylol ethane, and trimethylol propane, a polyester resin (including an oil-modified type) having a functional group which reacts with isocyanate group, an acrylic resin, etc., and water, etc., a buret compound, a polymer allowed to react between isocyanates, or an equimolar adduct of 2-hydroxypropyl (meth)acrylate-hexamethylene diisocyanate, a copolymer essentially containing a vinyl-based monomer which has an isocyanurate group such as isocyanatemethyl (meth)acrylate and a copolymerizable unsaturated group, or compounds described in JP-A-61072013 Official Gazette, and a blocked compound blocked by a blocking agent such as a lower monovalent alcohol, phenols, methylethylketoxime, and a lactam, etc.

The diisocyanates may be employed solely or even in combination

of two or more kinds.

From a viewpoint of a color tone in a coating layer obtained using the curable resin composition of the present invention, as a polyisocyanate compound, non-yellowing type polyisocyanates are preferred, and the following ones are disclosed as an example.

There are enumerated aliphatic-based polyisocyanates such as 1,4-tetramethylene diisocyanate, 1,5-pentamethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylenediisocyanate, and ridine diisocyanate; cycloaliphatic-based polyisocyanates such as isophorone diisocyanate, methyl cyclohexane-2,4-(or 2,6) diisocyanate, dicyclohexyl methane-4,4'-diisocyanate, and 1,3-bis(isocyanatemethyl) cyclohexane, and the above-described derivatives (including an adduct) therefrom. Of those, there are preferably enumerated 1,6-hexamethylene diisocyanate (hereinafter, abbreviated as HMDI), isophorone diisocyanate (hereinafter, abbreviated as IPDI), and a derivative (including an adduct) therefrom in view of weatherability and an ease of industrially-obtaining.

Since the polyisocyanate compounds reacts with polyols in a base material even at room temperatures, those include a problem that those are poor in storage stability, and handling is troublesome and, those are unpreferred in view of safeness and hygiene. Accordingly, blocked type polyisocyanates are preferred as the polyisocyanate compounds.

Although the blocked type polyisocyanates (hereinafter, occasionally referred to as a highly-branched block polyisocyanate) are obtained even only by allowing to react the polyisocyanates with

a polyvalent alcohol, more preferably, those can be obtained by cyclic trimerization of an isocyanate, that is, isocyanuration after allowing to react a diisocyanates with the polyvalent alcohol.

As the polyvalent alcohol in the case, there is preferred an alcohol having three or more functionalities and, as a polyvalent alcohol having a low molecular weight, for example, there are trimethylol propane, glycerine, 1,1,7-trimethylol heptane, 1,2,7-trimethylol heptane, and pentaerythritol, etc. As a polyvalent alcohol having a higher molecular weight, for example, there are enumerated aliphatic hydrocarbon polyols, polyether polyols, polyester polyols, and epoxy resins having a plurality of hydroxyl groups at terminals, etc.

As the aliphatic hydrocarbon polyols, for example, there are enumerated a polybutadiene having hydroxyl group at terminals and a hydrogenate product therefrom, etc. Further, as the polyether polyols, for example, there are enumerated so-called polymer polyols, etc. that is, polyether polyols or polytetramethyleneglycols obtained by adding alkylene oxides such as ethylene oxide or propylene oxide alone or in a mixture, and components obtained by polymerizing acrylic amides in media which are polyethers obtained by reacting alkylene oxides with polyfunctional compounds such as ethylenediamine or ethanolamines.

As the polyester polyols, there are enumerated polyester polyol resins obtained by condensation reaction of at least one of a polybasic acid with at least one of polyvalent alcohols and polycaprolactones obtained by ring-opening polymerization of ϵ -caprolactone using the polyvalent alcohols.

As the polybasic acid, for example, there are enumerated phthalic

acid (anhydride), terephthalic acid, isophthalic acid, tetrahydrophthalic acid (anhydride), hexahydrophthalic acid (anhydride), 4-methylhexahydrophthalic acid (anhydride), 3-methylhexahydrophthalic acid (anhydride), 3-methyltetrahydrophthalic acid (anhydride), trimellitic acid (anhydride), pyromellitic acid (anhydride), phthalic acid (anhydride), phthalic anhydride, adipic acid, sebacic acid, azelaic acid, succinic acid (anhydride), maleic anhydride, fumaric acid, itaconic acid, and a dimer acid, etc. The acid may be employed even in the form of an ester of a lower alcohol such as dimethylisophthalate and dimethylterephthalate.

The polyvalent alcohols are a compound having at least two alcoholic or phenolic hydroxyl groups in a molecule, for example, there are specifically enumerated ethylene glycol, diethylene glycol, triethyleneglycol, polyethyleneglycol, 1,6-hexanediol, pentanediol, cyclohexane dimethanol, propylene glycol, butylene glycol, butylene diglycol, trimethylol ethane, trimethylol propane, glycerine, neopentyl glycol, sorbitol, tris(2-hydroxyethyl)isocyanurate, diethanol amine, diisopropanol amine, bisphenol A, and bisphenol F, etc.

As the epoxy resins, for example, there are enumerated a novolak type, β -methylepichlorohydrin type, a cyclic oxirane type, a glycidylether type, a glycolether type, an epoxy type of an aliphatic unsaturated compound, an epoxidized fatty acid ester type, a polycarboxylic acid ester type, an aminoglycidyl type, a halogenated type, and resorcinol type, etc.

Of the polyols, there are preferably employed the above-described

polyvalent alcohol having a low molecular weight and a polyether polyol having 3-8 pieces of hydroxyl groups in a molecule, the aliphatic hydrocarbon polyols, and polyester polyols and, particularly preferably, the polyester polyols. These may be employed solely or in combination of two or more kinds. Aliphatic or cycloaliphatic diisocyanate and the polyvalent alcohols are allowed to react at 50-200°C, and preferably 50-150°C. In the case, solvents may be employed, and there are preferably employed solvents which are inactive to an isocyanate. As such the inactive organic solvents, for example, there are employed at least one kind of aliphatic hydrocarbons such as hexane, heptane, and octane, aromatic hydrocarbons such as benzene, toluene, and xylene, esters, and ketones. Since the solvents occasionally contain moisture, it is preferred to optionally remove the moisture. Although the reaction can be conducted even after an isocyanuration reaction, it is preferably conducted prior to the isocyanuration reaction.

In the isocyanuration reaction, catalysts are usually employed. The catalysts to be employed herein are preferably basic, for example, there are employed a quaternary ammonium salts and a weak organic acid salt thereof, an alkyl metal salt of an alkyl carboxylic acid, an metal alcoholate, and a compound having an aminosilyl group, etc. Concentration of the catalysts is usually selected from a range of 210 ppm to 1.0% based on isocyanate compounds.

In the reaction, solvents may be employed or even not employed. In the case that the solvents are employed, there should be employed solvents which are inert to an isocyanate group.

Reaction temperature is usually 20-160°C, and preferably 40-130°C. Termination point of the reaction depends upon the kind of the polyvalent

alcohols to be employed, and it is a period at which yield attains to approximately 30%. When the reaction attains to a target yield, for example, the reaction is terminated by deactivation of the catalysts by, for example, sulphonic acid, phosphoric acid, and phosphates, etc.

In a highly-branched polyisocyanate having an isocyanurate structure after removal of unreacted diisocyanates and solvents, viscosity at 25°C is preferably 0.5-300 Pas. In the case that the viscosity exceeds 300 Pas, outer appearance in a coating layer is adversely affected occasionally and, in the case of being less than 0.5 Pas, it is difficult to obtain a range of an average functional group number of the polyisocyanate regulated in the present invention.

As a blocking agent for obtaining the highly-branched block polyisocyanate, for example, there are enumerated phenol-based ones such as phenol, cresol, xylenol, ethylphenol, o-isopropylphenol, butylphenol such as p-tert-butylphenol, p-tert-octylphenol, nonylphenol, dinonylphenol, styrenized phenol, oxybenzoic acid phenol, thymol, p-naphthol, p-nitrophenol, p-chlorophenol; alcohol-based ones such as methanol, ethanol, propanol, butanol, ethyleneglycol, methylcellosolve, butylcellosolve, methylcarbitol, benzyl alcohol, phenylcellosolve, fulfurylalcohol, and cyclohexanol; active methylene-based ones such as dimethyl malate, diethyl malate, methylacetoacetate, ethylacetoacetate, and acetyl acetone; mercaptan-based ones such as butyl mercaptan, thiophenol, and tert-dodecyl mercaptan; amine-based ones such as diphenyl amine, phenylnaphtyl amine, aniline, and carbazole; acid amide-based ones such as acetanilide, acetoanisidide, amide acetate, and benzamide; lactam-based ones such as ϵ -caprolactam, δ -valerolactam,

γ -butyrolactam, and β -propiolactam; acid imide-based ones such as succinic acid imide and maleic acid imide; imidazole based ones such as imidazole, 2-methylimidazole, and 2-ethylimidazole; urea-based ones such as urea, thiourea, an ethylene urea; carbamide acid salt-based ones such as N-phenylcarbamic acid phenyl and 2-oxazolidone; imine-based ones such as ethyleneimine and a polyethylene imine; oxime-based ones such as formaldoxime, acetoaldoxime, acetoxime, methylethylketoxime, methylisobutylketoxime, and cyclohexanooxime; bisulphite-based ones such as sodium bisulphite and potassium bisulphite, etc., and these may be even as a mixture.

Of those, there are preferred the phenol-based ones, lactam-based ones, alcohol-based ones, and oxime-based ones and, there are particularly preferred nonylphenol, styrenized phenol, oxybenzoic acid ester, acetoxime, methylethylketoxime, and ϵ -caprolactam.

In the case that a low temperature (not more than 140°C) baking is demanded, particularly, an oxime-based blocking agent is most preferred.

By allowing to react the blocking agent with the highly-branched polyisocyanate, the highly-branched blocked polyisocyanate can be obtained. Reaction of the isocyanate with the blocking agent can be conducted regardless of the presence or absence of solvents. In the case that the solvents are employed, there should be employed solvents which are inert to an isocyanate group.

In the reaction for blocking, there may be even employed catalysts such as organic salts of metals such as tin, zinc, lead, and a tertiary amine, etc. The reaction can be conducted at -20 to 150°C and, preferably, 0 to 100°C. In the case of exceeding 100°C, side reactions are possibly

caused and, on the other hand, in the case of too low temperatures, reaction rate becomes slow, and it is disadvantageous.

The block polyisocyanate to be employed in the present invention has the number of average functional group of 4.5-10, preferably, 5-8 per 1 molecule of the block polyisocyanate.

The number of average functional group in the block polyisocyanate is a number of an isocyanate functional group to be statistically possessed in 1 molecule of the block polyisocyanate, and it is calculated by the above-described equation (1) from a number average molecular weight of the polyisocyanate before the blocking reaction and an isocyanate concentration (%).

As the above-described polyisocyanate compound to be employed as the hydrophobic crosslinked particles, there are typically enumerated a variety of toluene diisocyanate (TDI)-based polyisocyanates typified by a trimethylolpropane (TMP) adduct-prepolymer; a variety of hexamethylene diisocyanate (HMDI)-based polyisocyanates typified by a TMP adduct-prepolymer; (HMDI)-based polyisocyanates which are buret type HMDI-based polyisocyanates or an isocyanurate-prepolymer; isophorone diisocyanate (IPDI)-based prepolymers which are an isocyanurate-prepolymer; a variety of xylilene diisocyanate (XDI)-based polyisocyanates typified by a TMP adduct-prepolymer; or 4,4'-diphenylmethane (MDI)-based diisocyanates, etc.

In the above-described hydrophobic crosslinked particles, an epoxy resin can be simultaneously employed. Particularly, typical resins alone are exemplified, and there are enumerated "Epikote 828

or 1001" which is a bisphenol A type one manufactured by Yuka Shell, Ltd.; an epoxidized polybutadiene manufactured by Adeka Argus, Ltd.; "DEN431, 438, XD-7818, XD-7855, or DER331" which is a phenol-novolak type epoxy resin manufactured by Dow Chemical, Ltd.; "ECN268, 273, 280, 285, or 299" which is a cresol-novolak type epoxy resin manufactured by Asahi Kasei Kogyo, Ltd.; or multifunctional glycidyl amines or multifunctional glycidyl ethers, etc.

Further, as such the epoxy resins, there can be also employed copolymers having glycidyl groups obtained by copolymerization of glycidyl(meth)acrylate.

In the present invention, since urethane bonds produced by using the polyisocyanate compound can exhibit more excellent properties such as, above all, chemical resistance and hydrolysis resistance compared to other ether bonds and ester bonds, a mode of the present invention is particularly desired.

The acrylic polyol resin (VI-A) and the polyisocyanate compound (VI-B) in relation to the present invention construct an essential component in the curable resin composition of the present invention, and it is employed as raw materials for a coating.

There is decided an equivalent ratio of isocyanate groups or a blocked isocyanate group in the polyisocyanate with respect to hydroxyl groups in the resin having hydroxyl groups according to physical properties in a coating layer to be required.

The acrylic polyol resin (VI-A) obtained by using the hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones and the polyisocyanate compound (VI-B) are preferably formulated in a ratio of $\text{OH/NCO}=1/0.5-1/1.5$ (equivalent ratio) from

a viewpoint of characteristics in a coating layer. Above all, those are formulated in a range of $\text{OH/NCO}=1/0.7-1/1.2$ (equivalent ratio).

In the case that NCO is not more than 0.5 equivalent with respect to 1 equivalent of OH, there are not shown physical properties to be desired for a coating layer such as extensibility, weatherability, solvent resistance, and staining resistance and, in the case of not less than 1.5 equivalent, although the physical properties for a coating layer are obtained, it is not preferred from a viewpoint of readily bubbling under a high temperature, and a high price in a coating.

The curable resin composition of the present invention contains 20-90 parts by weight of the acrylic polyol resin (VI-A) obtained by using the hydroxyakyl(meth)acrylate composition modified by a small amount of lactones (a) and 5-50 parts by weight of the polyisocyanate compound (VI-B) as essential components, provided that total of the (VI-A) and (VI-B) does not exceed 100 parts by weight.

In the case that the acrylic polyol resin (VI-A) is less than 20 parts by weight, there lacks an amount of a hydrophilic portion taking charge of a water dispersibility, and there lowers a water dispersion stability and, in the case of exceeding 90 parts by weight, there become unpreferably worse workability and a water dispersibility. In the case that the polyisocyanate compound (VI-B) is less than 5 parts by weight, curability becomes insufficient and, on the other hand, in the case of exceeding 50 parts by weight, a cured coating layer becomes unpreferably too rigid or too brittle.

As use ratio of the acrylic polyol resin (VI-A) with respect to the polyisocyanate compounds (VI-C), the polyisocyanate compounds

(VI-B) are 60-10% by weight with respect to the 40-90% by weight of the acrylic polyol resin (VI-A). In the case that the use ratio the acrylic polyol resin (VI-A) is less than 40% by weight, a self-condensation reaction increases in the polyisocyanate compounds themselves, and coating layer becomes brittle, resulting in becoming not appropriate as a coating for, for example, a molded article from a polyolefine-based resin. On the other hand, in the case that the use ratio of the acrylic polyol resin (VI-A) exceeds 90% by weight, crosslinking becomes insufficient, and there lower solvent resistance and weatherability. A preferred use ratio of the acrylic polyol resin (VI-A) is 60-80% by weight and, accordingly, a preferred use ratio of the polyisocyanate compounds (VI-B) is 20-40% by weight. In the case that the use ratio of the polyisocyanate compounds (VI-B) is less than 20% by weight, curability becomes insufficient and, an intermolecular crosslinking density lowers and, as a result, there is readily caused a situation that there are not sufficiently shown characteristics by using the crosslinked particles. On the other hand, in the case of exceeding 40% by weight, a cured coating layer becomes too rigid and, emulsifying through phase inversion often becomes difficult or quite impossible. Accordingly, it is not preferred in both cases.

The present invention basically intends to provide a method for the preparation of crosslinked particles comprising dispersing and crosslinking a mixture of the acrylic polyol resin (VI-A) having carboxylic groups and crosslinkable functional groups with the polyisocyanate compounds (VI-B) (a hydrophobic crosslinking agent)